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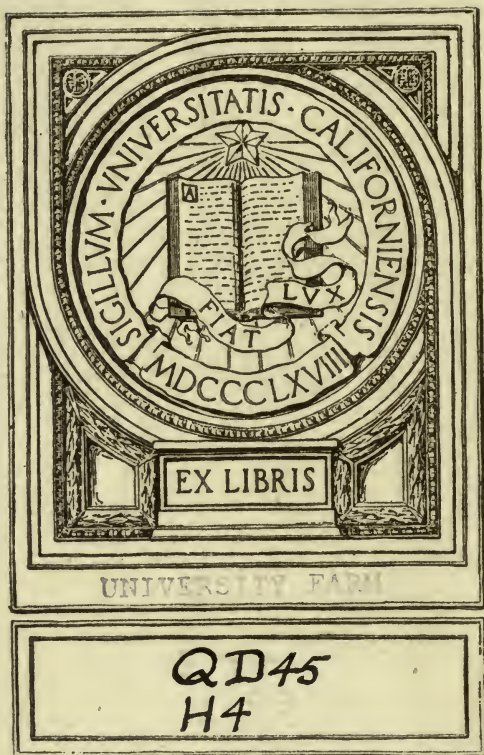


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A Laboratory Manual  
of General Chemistry

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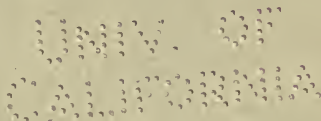
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A LABORATORY MANUAL  
OF  
GENERAL CHEMISTRY

BY

W. S. HENDRIXSON,  
Professor of Chemistry in Grinnell College.

GRINNELL, IOWA,  
1918



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## PREFACE.

This the fourth edition of the author's Experiments in General Chemistry is printed, as its predecessors have been, primarily for the use of students in general chemistry in Grinnell College. This fact may explain certain departures from custom in the preparation of such books, such as suggestions to teachers and detailed descriptions of apparatus and its manipulation. As a matter of fact apparatus at all complicated is not only shown by cuts, but it is set up on the lecture table and many experiments for any period are there carried through before the students enter the laboratory. Some apparatus is even set up in the laboratory and left there for inspection during the laboratory period.

Not satisfied to use the same set of even his own experiments year after year and wishing to provide new laboratory work for classes of students who have taken chemistry in the high school, the writer has provided for more laboratory work than can be done in a three- or four-hour course of one year.

In this book an attempt is made to connect rationally general chemistry and qualitative analysis. Students who complete a first year course in chemistry should have some knowledge of qualitative analysis, but it should not be permitted to take the place of general chemistry in the second half year, which is usually devoted to study of the metals. Qualitative analysis ought to be a development from the general chemistry to which it gives point, and its introduction as an outgrowth of the general chemistry greatly stimulates the student's interest in both subjects. In this book tests for acids and other compounds are given in the study of the non-metals, and a system for the detection of acids is given after the study of the non-metals has been completed. In the study of the metals emphasis is placed on properties that are of analytical significance, though other facts are not neglected. After each group of metals has been studied their separation is taken up, and the work is extended as rapidly as the student's experience justifies it; to the detection of both metals and acid radicals in "unknowns." The scheme of qualitative analysis as outlined is not supposed to be complete but is meant to serve as an introduction to the subject and a preparation to the more rigorous course in qualitative analysis the following year.



## TO THE STUDENT.

I.—On coming to the laboratory the first day find the number of your desk, get the key or combination and a printed list of the apparatus the desk should contain. Verify the apparatus, asking the names of the things you do not know. Make sure that apparatus is wanting before calling for it. Present broken or faulty apparatus for exchange.

II.—After using apparatus, clean it and return it to the desk. Clean the top of the desk and lock it before leaving. Have old cloths for cleaning and a towel for the hands. In grading notes you will be held responsible for the condition of the desk without and within and for the bottles on its shelves, which should always be kept in the same order.

III.—Provide an approved note book of the sort shown in the lecture room. Leave the first leaf blank and enough margins to permit corrections by the instructor.

Begin every experiment on a new page. Write notes in the laboratory in full and do not copy them. Only original notes made while doing the laboratory work are of value. The notes on each experiment should have a suitable heading and should have the same number as the experiment. Paragraph to suit the subject matter. Present the note book for grading and criticism before leaving the laboratory.

IV.—Ascertain in advance what the laboratory work is to be for each period and prepare for it before coming to the laboratory by use of the text or reference book. The subject will be announced in the class room, and references to books will be given. Bring the text-book to the laboratory.

V.—Every experiment is intended to teach something of value. Try to find out what it is by yourself, using observation and the text-book, then ask the instructor. State results in the notes. Do not confine these efforts merely to answering the questions of the laboratory book. For example after equations have been studied in class all equations for reactions in the laboratory work should be written whether asked for or not. Write them where they belong scattered through the notes and do not write them in mass at the end of the notes.

VI.—When using chemicals replace the covers or stoppers of the containing vessels. Do not throw stoppers upon the desk. Return all bottles to their places on the shelves. Replace all weights in the boxes.

VII.—Do not wash pieces of apparatus with distilled water but with hydrant water. If they are well drained it will not be necessary in most cases even to rinse them with distilled water. On the other



hand always have distilled water in your wash bottle and use it in making all solutions.

VIII.—Throw no solid matter into the sinks but into the jars provided for that purpose. On the other hand wash apparatus at the sinks and do not throw large amounts of water into the jars.

### DIRECTIONS FOR LABORATORY WORK. GENERAL MANIPULATION.

**1.—The Bunsen Burner:** Take apart the burner and study its construction. Determine how to regulate the supplies of gas and air. Put it together and turn on the gas at the cock and regulate the supply by the screw on the burner. Regulate the gas and air so as to secure a non-luminous flame. Too much air may cause the flame to blow out, "snap back" or burn with much noise. A long green hissing flame indicates that the gas is burning also at the base. Turn out the flame, reduce the amount of air, light again. A flame about 3 inches long is usually sufficient.

The ordinary flame is used to heat test tubes directly, or to heat such as flasks and beakers placed upon wire gauze, of which nichrome gauze is best. The crown top is used to heat beakers and flasks without protection of gauze.

**The Wing Top:** Put the wing top on the burner, turn on the gas and regulate gas and air so as to secure a just non-luminous flame about as high as broad. Too much air is objectionable. Such a flame should be used exclusively for bending tubing.

**2.—Breaking and Bending Glass Tubing:** Draw once a sharp, three-cornered file across the piece of tubing where you wish to break it. Hold the tube with both hands, with thumbs together and opposite the scratch. A slight pull will break the tube squarely at the scratch.

To bend glass tubing **always use the wing top.** No one but an expert can make a good bend with the flame of the ordinary burner. A bend so made will be uneven, crinkled and the tube is likely to break at that point.

Hold the tube above the middle of the wing flame, having its length in direction of the breadth of the flame. Revolve the tube and move it back and forth in the direction of its length until it softens and begins to yield to a slight pressure, then bend it slowly as desired. If it shows a tendency to collapse or flatten at any point, stop bending at that point, heat at one side or the other and there complete the bend. The tendency to collapse shows that the bend is being made too short. Practice with scraps of tubing until you can make a good bend, and then make the tubes like the samples shown in fig. 1. They represent the tubes most used in this course, and should be kept

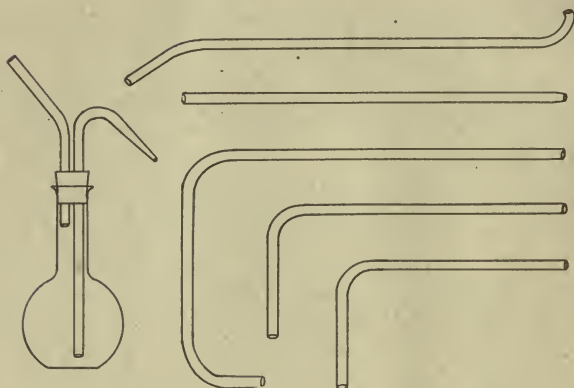


Fig. 1

throughout the year and not cut up to make other things. Heat the ends of the tubes to redness in the ordinary flame to fuse down the sharp edges. Other glass working will be shown in the class room as occasions arise.

If there is no wash bottle in the desk construct one as shown in fig. 1. This wash bottle should always contain a supply of distilled water and should not be torn down to use the tubes or flask for any other purpose.

**3.—Weighing.** The following may be applied to all balances and weighings, but will be supplemented by the instructors when weighings of great accuracy are required.

Never place chemicals, other than pieces of metals, directly upon the pans of the balance, but in some suitable containing vessel. When only moderate accuracy is required, balanced papers may be used, but not where accurate weighings are called for. In the latter case two methods are good. Place a dish on the left hand pan and weigh it accurately. Place in it about the desired amount of substance and weigh again. Of course the difference between the weights gives the weight of the substance. The scales rarely "balance" or the pointer rarely stands at the zero point. This error, however, is eliminated by the above method. Instead of the dish, the substance may be weighed in a corked tube, then the desired amount may be taken out and the tube weighed again. Of course in both weighings the tube must be in the same pan, always the left.

When equilibrium has been attained, that is, when the pointer makes excursions equidistant right and left from the center, count the weights without removing them from the pan, record the weight in the

note book and verify by counting the weights again as they are removed to the box. Write the weight in the book as one number. If the weights are 5 g., 2 g., 200 mg., 50 mg., write the total at once 7.25 grams. Unless the nature of the experiment requires it, it is a mistake to try to weigh a definite amount of a substance. For example, if the directions say "Weigh accurately about 5 grams of the substance," do not try to get just five grams, but take about five grams and weigh it accurately.

**4.—Measuring Volumes of Liquids:** Study a pipet and a graduated cylinder. Why is the cylinder graduated from the top downward and from the bottom upward?

Weigh accurately a small flask on the horn-pan scales observing the directions given under weighing. Now put a small piece of rubber tubing on the larger end of the pipet, by suction fill it with distilled water to above the mark and pinch the rubber tube. Carefully let out the water to the mark and then run the remainder into the flask and weigh again. Find the weight of the water, the weight of 1 cc. and the error in the pipet according to your work. Why in this experiment does it make little difference whether the balance with pans empty was in exact equilibrium or not?

## OXYGEN.

**5.—Preparation of Oxygen:** (Study text-book in advance). Many substances containing it give off all or a part of their oxygen when heated. The following are illustrations:

In a small test tube heat about half a gram, estimated, of potassium chlorate. It melts and then seems to boil owing to the evolution of oxygen. Light a splinter or tooth pick, blow out flame, lower glowing end into the test tube. It should rekindle.

In another small tube, preferably one made of "hard glass" tubing heat a little mercury oxide persistently and test with glowing splinter. Note sublimed mercury on wall of tube. By persistent heating all the mercury oxide may be decomposed into mercury and oxygen.

As in the case of mercury oxide heat a little manganese dioxide and test for oxygen. Only one-third of the oxygen is given off.

Oxygen may be obtained also by heating lead dioxide, potassium permanganate, potassium perchlorate, barium dioxide to redness.

All these instances illustrate chemical change, and the nature of the change is that of decomposition.

**6.—Preparation of Oxygen, Laboratory Method:** (a) Read through the experiment and have everything required within reach. Set up the apparatus as shown in fig. 2, having trough filled with water to about 2 inches above the shelf. Place the delivery tube well to the farther side of the trough so as not to be obliged to reach over it.

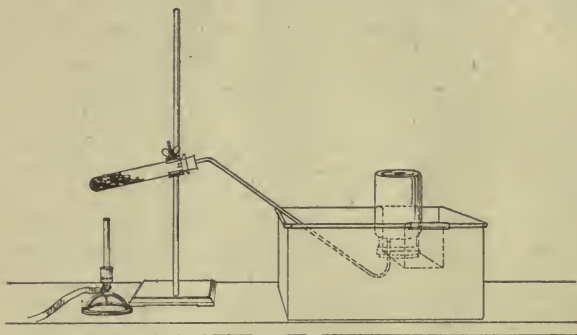


Fig. 2.

Fill two jars\* with water by immersing in the trough with mouth slightly upward, inverting them and placing upon the shelf as shown. Direct the base of the retort stand backward so that it will not be in the way of the burner. (See fig. 2). There is no need of clamping the test tube tightly so as to endanger breaking it. Have the clamp near its mouth. Why?

Weigh approximately on platform scales 8 grams potassium chlorate and 4 grams powdered manganese dioxide, mix them on paper with a spatula and from the paper slide the mixture into the test-tube.

Now heat the substance in the tube slowly and evenly, best by holding the burner in the hand and moving it back and forth along the tube, so as to avoid over-heating and softening the tube at any one point. So regulate the heat that the gas shall be coming off slowly when the jar is about full. When the jar is full slide it to one side and place another jar over the mouth of the tube, then place the cover securely on the full jar keeping its mouth under water, remove it to the desk and clamp on the cover. Fill five jars or bottles. When the gas ceases to come off remove the stopper of the tube to prevent a back flow of the water. Allow the tube to cool and meantime use the oxygen in 7. Return then to (b).

(b) Prepare a funnel with filter paper. Fold a filter in halves, then in fourths, open out one thickness making a cone, press down evenly into a funnel and wet it with water to make it hold its shape. Fill half full of distilled water the tube used to heat the potassium chlorate and manganese dioxide, and when the residue is wet throughout by shaking heat to boiling and filter by pouring the contents into the filter, being careful not to run it over, and catch the clear liquid, filtrate, in a large test tube or beaker. If not clear run it through again. To a little of the clear filtrate in a clean test tube add a few

\*Rubber seal, pint fruit jar.



drops of solution of silver nitrate. Now add a few drops of dilute nitric acid. The white **precipitate** is silver chloride. The formation of this white precipitate by silver nitrate in the presence of nitric acid is a much used test for a chloride. Make solutions of potassium chloride and potassium chlorate from the shelf bottles, add a little dilute nitric acid to each, then silver nitrate. Which gives silver chloride? What does your clear filtrate seem to contain? Evaporate a little of it to dryness in a porcelain dish. Compare the appearance and taste of residue with potassium chloride and chlorate from shelf. What chemical change took place on heating potassium chlorate? Was the manganese dioxide changed chemically on heating? For the use of manganese dioxide as a "catalyzer" see (8).

**7.—Properties of Oxygen:** Place about half a gram of sulfur in a deflagration spoon, best covered with a bit of asbestos paper, ignite the sulfur and lower it into a jar of oxygen. When the combustion ceases, add a little distilled water to the jar and shake. Test the water with blue litmus paper. The change to red shows acid formed by the union of water with sulfur dioxide produced by the combustion.

Ignite a piece of charcoal on a clean spoon and lower into a jar of oxygen containing a little water. Cover jar, shake and test the water with blue litmus paper. A faint red should be given the paper showing the formation of carbonic acid. Add to the jar clear lime water\* and shake. The milky appearance is due to calcium carbonate, produced by calcium hydroxide in the lime water and carbon dioxide.

Place a little red phosphorus on asbestos paper in the spoon, light it and quickly lower into oxygen. Test the water in the jar with blue litmus paper. Phosphorus pentoxide is first formed and this unites with the water forming phosphoric acid. What is an element? All three of the substances burned are elements. These are non-metals, and such on combustion usually form oxides that are acidic or unite with water to form acids.

Heat the end of a piece of picture wire, dip into powdered sulfur for an instant. A portion of the S will adhere and burn. Lower it into a jar of O. The sulfur burns and then the iron burns with a shower of sparks.

Without removing the kerosene which adheres to it place a bit of sodium as large as a grain of wheat in a spoon, ignite the kerosene and lower into a jar of oxygen. The kerosene should burn and ignite

\*If lime water is not present in the laboratory in quantity, it may easily be prepared by shaking a little slaked lime in a jar of water for some time, letting the lime settle and filtering. The funnel should be placed in a flask to protect the filtrate from carbon dioxide in the air.

the sodium. Shake the bottle and test the water with red litmus paper. The so-called alkali metals such as sodium burn and form oxides which unite with water forming an alkali.

The burning of these elements forming compounds, **oxides**, illustrates chemical change, and chemical reactions of the type called direct combination or synthesis.

**8. Manganese Dioxide as a Catalyzer:** In a test tube heat about 1 gram of potassium chlorate till it melts and begins to give off oxygen. Without cooling drop a very little manganese dioxide upon the fused salt. Is there much change in the rate of giving off oxygen? Compare temperature required when oxygen is prepared from a mixture of potassium chlorate and manganese dioxide, and from potassium chlorate alone. The next experiment illustrates further the influence of catalyzers, and also a very good method of preparing oxygen.

**9.—Oxygen from Sodium Dioxide (Peroxide):** In each of three dry test tubes place about a gram of sodium dioxide. In one place also a very little fine copper oxide and in another powdered manganese dioxide. In each of the three pour about 5c.c. of water and note rates at which oxygen is given off.

To prepare a larger volume of oxygen by this method set up the apparatus as in fig. 10, but use a dry flask instead of the test tube. Place in flask about 10 grams of sodium dioxide, then about half a gram of powdered copper oxide or manganese dioxide, shake to mix and spread the mixture evenly over the bottom of the flask. Fill the funnel with water and by means of the pinch cock let it run in slowly so as to maintain a suitable flow of oxygen. No heating is necessary. The oxygen may be tested with a glowing splinter. Sodium hydroxide, NaOH, is formed at the same time. Test a little of the solution in the flask with red litmus or turmeric paper. Test sodium hydroxide from the shelf with the same paper.

## HYDROGEN.

**11.—(a).** In as many test tubes place bits of magnesium turnings, aluminium turnings or wire, zinc, iron filings, or other finely divided iron such as steel wool; tin, copper, lead. To each tube add dilute hydrochloric acid. In what cases is hydrogen, a colorless gas, given off? In cases where it is not, add a few drops of concentrated hydrochloric acid. If some metals still resist warm the acid.

**(b).** In clean tubes and fresh metals try the same series with dilute sulfuric acid warming where necessary. In text-book refer to "electro-motive series." From the more electro-positive end of the series the metals give off H with decreasing readiness till hydrogen itself is reached. The metals beyond or below H do not give H with acids. That is, the metals that are more electro-positive than H dis-



place it from solution. There are secondary reasons why some metals above H do not evidently replace hydrogen. Lead is an example. (c). For the action of nitric acid on metals see 52.

**12.—Preparation of Hydrogen. Caution:** Mixtures of hydrogen and oxygen and hydrogen and air are dangerously explosive. In the

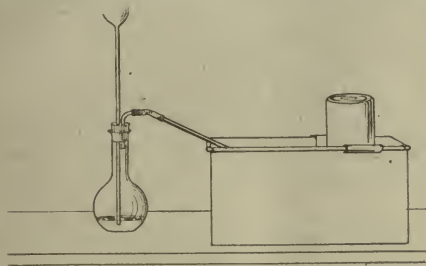


Fig. 3.

used in lighting the gas the second time.

In a small flask fitted as in Fig. 3 place about 25 grams of granulated zinc and about 50c.c. of dilute sulphuric acid. Add a few drops of a solution of copper sulphate if the action proceeds too slowly when sulphuric acid is used. To get the crystals mentioned below it is necessary to use sulphuric acid. In performing the experiment subsequently, instead of dilute sulphuric acid the zinc may be covered with water and then strong hydrochloric acid cautiously added through the funnel tube until the gas comes off freely. Collect the gas in jars rejecting the first jar full. Why? Collect two jars and then light the gas with a test tube of burning gas. That is, hold the delivery tube upward, and place over its end a small test or specimen tube. The hydrogen will rise and force the air downward. When the tube has had time to fill move it mouth downward to a flame, which should be a foot or two removed, and the H will light with a slight noise if pure. Carry the tube back and lower it for an instant over the delivery tube. Hold the flame inside the mouth of a dry bottle and continue until the liquid deposited collects in drops. Taste it and test it with litmus paper. What is it? In case the evolution of gas becomes too slow it is due to exhaustion of the acid and the accumulation of zinc sulfate, or chloride if hydrochloric acid was used. Merely adding more acid does not suffice. It is better to pour off the solution and replace it with fresh acid as in the beginning.

Fill a jar by pouring hydrogen upward into it from another jar and prove the presence of H in the jar by applying a flame to its mouth.

Hold a jar of H mouth downward, remove cover and insert a bit of lighted candle held on the end of a file or wire. Remove

preparation of hydrogen in this experiment and elsewhere have no flame near the delivery tube until all air is expelled from the flask. The gas should be lighted the first time with a test tube of burning gas. Should the stopper of the flask be removed so as to permit the entrance of air, the same precaution must be

candle when it will light again. Repeat several times. Does a candle burn in hydrogen?

When the evolution of gas in the flask has nearly ceased filter the liquid into a dish. If sulfuric acid was used crystals of zinc sulfate will appear when it becomes cold, or after it has been evaporated down one half and cooled again. If hydrochloric acid was used evaporate to dryness to obtain zinc chloride. Place some of it on a glass plate and observe at the next period. Is it hygroscopic?

**13.—Hydrogen from Water:** (a) Sodium should be handled with the forceps or dry hands. Press a piece of the metal tightly into a 22 cartridge shell. Fill a test tube with water, drop the shell into the trough and collect the gas by displacement of water. Test the gas for hydrogen.

(b) Set up the apparatus as shown in fig. 4 using a half inch gas pipe at least a foot long. Put near the middle of tube about 10 grams iron turnings held in place by loose plugs of steel wool. To protect the stoppers wrap cotton around the ends of the tube and keep it saturated with water. Use a very small flask and only 10c.c. of water in it. Heat strongly the middle of the iron tube and after several minutes boil the water in flask. After the air has been driven out of the tube collect and test the hydrogen. Prevent a back flow by removing delivery tube from the trough before removing burner from the flask.

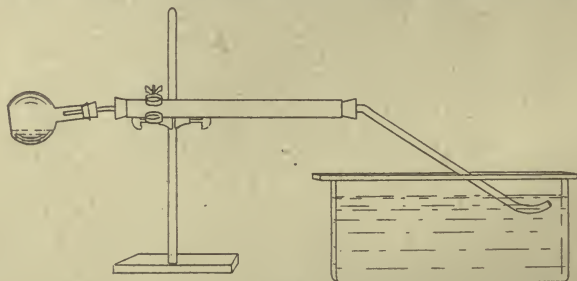


Fig. 4.

The experiment may be continued till a large amount of the iron is oxidized when it may be used in 14b; or, when cold more of the iron may be "rusted" by wetting it and putting aside for a day or two. It may then be heated and dried with a current of air before use in 14b.

In this experiment the reaction is shown from left to right:



while in 14b it goes from right to left, if the contents of this tube or magnetite is there used as provided for.

**14.—Hydrogen as a Reducing Agent:** The experiment may be performed as in (a) or (b).

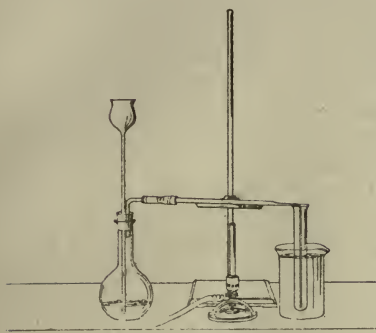


Fig. 5.

(a) Place in a piece of hard glass tubing a column of granulated copper oxide using loose plugs of asbestos to hold the oxide in place. The tube may be drawn out and bent at right angle as shown in Fig. 5 or a small right angled tube may be connected with its outer end by rubber. Connect with the flask which contains zinc, and add dilute sulphuric acid. Turn the small tube upward and determine when the air is wholly expelled by lighting the hydrogen with a test tube as in Ex. 12. Now turn the tube downward, place it in a test tube surrounded with water and heat the copper oxide, beginning at the end of the column nearer the flask. Continue till the copper oxide is all reduced, that is, all changed to red copper. Examine the liquid that has collected in the test tube. What is it?

(b) For the glass tube and copper oxide in (a) substitute the iron tube and contents from (13b) or use the iron tube and about 5 grams of ferric oxide. First fill the tube completely with hydrogen as proved by lighting it with a test tube, heat the oxide strongly, protecting the stoppers with the wet cotton as stated in 13b.

With a moderate flow of hydrogen continue the reduction 10 to 15 minutes. What is the source of the water in the test tube? When cold and if ferric oxide was used test some of the contents of the tube in con. HCl warming. What gas is evolved? What evidence have you that the reaction in 13b is reversed? What is a reversible reaction? What governs the direction of this one? How could you produce a state of equilibrium in it? What is the meaning of equilibrium?

## WATER.

**15.—Solubility of Solids:** Some substances are very soluble in cold, still more soluble in hot water. Shake 3 grams of powdered sodium nitrate or ammonium chloride with 5c.c. of water in a test tube till all is dissolved. Is there any change in temperature of the water? Now add 3 grams more and shake. Shake and determine whether it all dissolves. If not, heat till dissolved. What occurs on cooling to room temperature?

Some substances are very soluble in hot water, slightly in cold water, and such may easily be purified by crystallization from hot solution. By heating dissolve 4 grams of ordinary potassium chlorate in 10c.c. distilled water. Filter boiling hot if there is any turbidity or

solid matter suspended in the liquid. When the solution is cold filter off the crystals, setting filtrate aside and wash crystals with a little cold water, dissolve a portion of them in distilled water and add silver nitrate to the solution and to filtrate. Compare the amount of precipitate obtained with silver nitrate in the two tubes. It is due to a chloride, commonly found in ordinary potassium chlorate.

Some substances are little more soluble in hot water than in cold water. Shake 5 grams of common salt with 10c.c. of water in a test tube. Note the amount of salt undissolved. Boil the solution for a few moments to saturate the water with salt. Note again the amount of salt. Filter the solution boiling hot and cool to room temperature. Does much salt crystallize out? Why not? Compare the solubility of salt in hot and cold water with that of potassium chlorate. A few substances are even less soluble in hot water than in cold. Examples are calcium sulfate (gypsum) and slaked lime.

**16. Solubility of Liquids in Liquids, and the Separation of Solutes between two non-miscible Solvents:** Measure accurately in a cylinder about 50c.c. of water reading at the lower surface of the meniscus. Now carefully pipet into the cylinder 25c.c. of common alcohol. Mix thoroughly and read the volume. Is the volume now the sum of those of the alcohol and water? Do water and alcohol dissolve each other completely?

In a test tube place about 10c.c. of water and about 2c.c. of chloroform and shake. Let stand and note whether they are mixed. Add a crystal of iodine and shake for some time and let stand. Which liquid takes up most of the iodine?

As above try to mix 10c.c. of water and 2c.c. of carbon disulfide. Add about 5c.c. of bromine water and shake. Which liquid takes up most of the bromine?

To another tube add water and a little benzene, and a small crystal of potassium permanganate and shake. Which liquid takes up the permanganate?

Determine whether alcohol and chloroform, benzene and chloroform, carbon-disulfide and benzene will mutually dissolve each other.

**17—Solubility of Gases:** Gases also vary widely in their solubility in water. In text-book see solubility of oxygen, nitrogen and hydrogen sulfide which do not act chemically with the water, dissolve only moderately and obey Henry's law, (which see). Others which generally act chemically with water dissolve in very large amounts.

In a test tube or flask heat hydrant water and observe gas bubbles given off before the water begins to boil. Try the same with distilled water. Does it contain dissolved gases. Why does water when drawn from the hydrant sometimes look milky and quickly become clear on standing?



Note carefully the odor from a solution of ammonia due to ammonia given off. Pour about 1c.c. of the solution into 10c.c. of water in a dish and test with turmeric paper. Boil till the water is half evaporated and test again with the paper. What is the effect of heat on the solubility of gases. To a degree the following shows one of many exceptions to the general rule:

Boil 10c.c. of dilute hydrochloric acid till three-fourths of it has evaporated. Boil the same volume of concentrated hydrochloric acid till one half has evaporated. Add to each sample of boiled acid when cold, the same amount of granulated zinc. Do they seem to act on zinc at about the same rate? A more accurate determination would show that they have the same concentration. By boiling long enough samples of dilute and concentrated hydrochloric acids one arrives at the same result; namely acids of concentration 20.2 per cent.

**18.—Chemical Action of Water:** Refer back to 13 for the action of water on sodium and on iron, and to 9 for its action on sodium dioxide.

Upon a piece of quick lime drop water slowly until the water is no longer absorbed and the piece of lime looks wet. Place it in a dish and note what occurs. This is the familiar "slaking" of lime.

**19.—Water in Combination:** In a test tube heat a small amount of copper sulfate, observing water given off and changed appearance. In the same way try borax, alum, sodium phosphate. These are "hydrates" and the water they contain is called "water of crystallization." For contrast try potassium sulfate and common salt.

In a weighed porcelain crucible with lid weigh accurately about 4 g. of barium chloride, place the crucible on a triangle over a burner and heat ten minutes. When cold weigh the crucible and contents again and from the first weight of the barium chloride and the loss on heating, calculate the per cent. of water.

**Efflorescence:** On a glass plate or watch-glass place a few crystals of sodic sulphate, expose to air till the next laboratory period.

**Deliquescence:** Expose to air in dishes small pieces of calcium chloride and caustic potash till the next laboratory period and record results.

**20. Electrolytic Decomposition of Water:** Support the U tube shown in fig. 14 with a clamp and use the current described in 53. Connect the side-arms of the tube with the trough of water by means of short delivery tubes. Fill the U tube nearly to the side arms with a 5th normal solution of sodium sulfate already made up and add a few drops of litmus solution to each side of U tube. Start the current and at the same time place over the ends of the delivery tubes two test tubes the same size and full of water, thus collecting the hydrogen and oxygen set free. Continue till the smaller volume equals about 5c.c.

and compare volumes. Note color of the solution at each electrode and state cause. Name electrodes. From which comes the O, and the H?

**21. Purification of Water by Distillation:** To a small volume of hydrant water add a few drops of barium chloride solution. The white precipitate shows carbonate and sulfate radicals present. Now add dilute hydrochloric acid. The precipitate remaining shows sulfate radical. To another portion add a few drops of dilute nitric acid and a few of silver nitrate. A white precipitate shows chloride present.

Set up apparatus shown in fig. 6, fill flask one-third full of water, distill enough to clean the tubes and reject it. Distill about 10c.c. of the water and test it for sulfate and chloride radicals. None should be obtained, all ordinary mineral matter being left in the boiler in distillation.

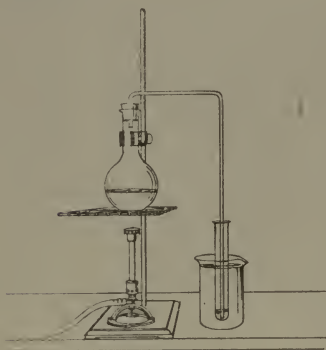


Fig. 6.

Try the action of ammonia and sodium hydroxide on turmeric paper and dilute sulfuric acid on blue litmus paper. To one-fourth of flask full of water add about 5c.c. of ammonia, distill and determine whether any ammonia distills over. Clean apparatus carefully and try sodium hydroxide, adding a few c.c. to one-fourth flask of water. Distill from a fresh portion of water containing a little sulfuric acid and a little potassium permanganate. Do they go over?

### HYDROGEN DIOXIDE (PEROXIDE).

**22.—Preparation:** Place a beaker with 100c.c. of water in water, preferably ice cold. Stir in little by little 5 grams of sodium dioxide,  $\text{Na}_2\text{O}_2$  the operation taking about 5 minutes. Even then some of the peroxide will be decomposed giving off oxygen. Now add gradually in the same way dilute hydrochloric acid till a drop of the liquid taken out with the stirring rod just turns blue litmus paper red. This gives a solution of hydrogen peroxide, but it contains also common salt. It may be used where hydrogen peroxide is required below save where it is used with silver and lead. There the commercial peroxide should be used.

Rub in a mortar with a little water about half a gram of starch, transfer to a dish or beaker, add about 100c.c. of water and a few crystals of potassium iodide and heat to boiling. This is known as "starch-iodide solution" and filter paper wet with it is called "starch-iodide paper." Each is frequently required. To a part of the solution add a



few drops of the solution of hydrogen peroxide which sets free iodine and this colors the starch blue. To see the color by transmitted light dilute with much water. This is used as a test for iodine or hydrogen peroxide or starch. That is, two being known to be present the presence or absence of the third can be determined by the test.

**23.—Oxidation with Hydrogen Peroxide:** Moisten a strip of filter paper with very dilute lead acetate and expose it to hydrogen sulfide a little of which may be made in a test tube as in 68. The black substance is lead sulfide,  $\text{PbS}$ . Pour upon the paper a few drops of hydrogen dioxide, which will change the lead sulfide to white lead sulfate,  $\text{PbSO}_4$ . Why is this called oxidation?

To a solution of silver nitrate add  $\text{NaOH}$  and then carefully add just enough of a solution of ammonium hydroxide to dissolve the precipitate at first formed. Now add commercial hydrogen peroxide. The gray precipitate is finely divided metallic silver, and the escaping gas is oxygen which may be tested by trying in the tube a glowing splinter. This action appears to be one of reduction, but it is not primarily. Probably a higher oxide of silver is formed and at once decomposes into silver and oxygen. The next two cases are of the same sort.

To about a gram of manganese dioxide in a test tube add hydrogen dioxide and test the gas with a glowing splinter. Repeat using a concentrated solution or a few crystals of potassium permanganate instead of the manganese dioxide.

## CHLORINE.

**24.—Preparation of Chlorine:** Chlorine is dangerous if breathed. Experiments with it should be conducted in hoods. If carried out on the students' desks only half the usual number should work in the room at one time and windows should be freely opened. They should stand to windward of the apparatus when collecting the gas. When through collecting at once place the delivery tube in a test tube nearly full of concentrated sodium hydroxide, and remove the source of heat. Before beginning the experiments students should read them through, the right plan in any case, provide everything necessary and thus reduce the time to the minimum. Make a solution of starch-iodide as directed in 22.

Chlorine is made commercially by the electrolysis of fused common salt or a solution of common salt. All other methods depend upon the oxidation of the hydrogen of hydrochloric acid. Several methods may be illustrated on a very small scale.

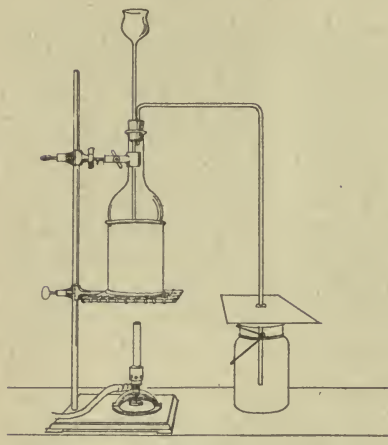


Fig. 7.

25.—Set up the apparatus as in fig. 7, with the water bath one-fourth full of water. A copper can is best, but a tin can or a beaker will serve for a water bath. See that the thistle tube reaches nearly to the bottom of the flask. In the flask place 25 grams of manganese dioxide  $\text{MnO}_2$ , and add 40c.c. of concentrated  $\text{HCl}$  diluted with 10c.c. of water. Heat the flask and collect five jars or bottles of chlorine. The green color will show when they are full. They should be well filled, but a large excess should not over-flow into the room. One jar should have the bottom wet with con. sulfuric acid to dry the gas for use in bleaching.

When through collecting place the delivery tube in  $\text{NaOH}$  in a test tube. Let the flask cool, removing water bath, and proceed with the next experiment.

26.—**Properties of Chlorine:** To show bleaching action and the need of water, suspend in the jar of dry chlorine strips of colored cotton cloth and litmus paper. After a few moments note any fading of the colors, then moisten the strips and suspend again in the jar, and note effect. Refer to a text-book for information on hypochlorous acid and bleaching with chlorine. What does the bleaching?

Into a jar of chlorine pour successively with shaking, small volumes of solutions of litmus, cochineal, much diluted ink.

From a piece of antimony scrape with a knife a very little of the metal letting it fall into a jar of chlorine. Using forceps or tongs heat to redness a strip of copper foil and lower it into the same jar of chlorine. If "Dutch metal" is used it need not be heated.

Upon a few crystals of potassium permanganate in a test tube pour about 1c.c. of con. hydrochloric acid and pour a little of the heavy, greenish yellow gas into a little of the starch solution in another tube. In the same way treat a little potassium dichromate heat and test for chlorine. Try in the same way lead dioxide and con. hydrochloric acid. Use a **very little** potassium chlorate and concentrated hydrochloric acid,  $\text{HCl}$ ; also, about 1 cc. con.  $\text{HCl}$  and a few drops of con. nitric acid.

Burn the laboratory gas at the end of a glass tube and lower the small flame into a jar of chlorine. What is the black substance? When the green color has disappeared blow breath over mouth of jar, which will give a fog, consisting of droplets of water containing HCl. Will carbon burn in Cl? Try an ignited piece of charcoal.

On a deflagration spoon lower a small bit of white phosphorus into a jar of Cl and avoid inhaling the Cl or fumes of  $\text{PCl}_3$ . It should soon melt, then take fire.

Now take the flask and all jars to the sink best under hood and standing well back fill them with water. Wash well any remaining  $\text{MnO}_2$  and place it in a vessel provided for that purpose.

### HYDROCHLORIC ACID.

**27.—Preparation:** Read the experiment through and have all the necessary materials at hand so that once begun the experiment may be carried through rapidly.

All soluble chlorides give hydrochloric acid when treated with concentrated sulfuric acid. For many reasons sodium chloride, common salt, is to be preferred.

Set up the apparatus as in fig. 7, omitting the water bath. In the flask place 20 grams of sodium chloride. Dilute 35 grams (20c.c.) of concentrated sulfuric acid by pouring it slowly with stirring into 8c.c. of water in a beaker. Pour slowly into the flask and let stand a few moments till acid and salt are in contact throughout then apply a low heat, best using a burner with crown top. Collect the gas in dry jars or bottles in the same way as chlorine. Abundant fumes will indicate when the jars are full. After collecting two jars, fill a dry bottle which has been fitted with a stopper and a short piece of tubing one end flush with the large end of stopper and the other drawn out and cut off so as to leave a small orifice. It should reach at least to the middle of the bottle's length. Insert stopper when full and place the bottle mouth downward in water. Press down the bottle and pour cold water over it to start the absorption. A fountain will result.

Into a test-tube of water insert the delivery tube so that it reaches a very little below the surface of the water. Note ready absorption of the gas. Is the solution lighter or heavier than water? Lower the tube as necessary to absorb all the gas. Why does the water become warm? Continue till the water is nearly saturated, then try the action of small portions of the solution on a little zinc, marble, sodium carbonate. Compare its action with that of the dilute HCl from the shelf. Test its action on blue litmus paper. To a little of the solution add a few drops of silver nitrate then a few drops of dilute nitric acid. The precipitate is silver chloride. This is a test for hydrochloric acid or a chloride. Repeat using instead of HCl a few drops of a solution of

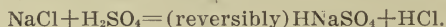
salt or of any other chloride. With a known chloride could it be used as a test for silver? Save flask and its contents for 29.

**28.—Acid, Base, Salt, Neutralization:** Wet the inside of a jar with a solution of concentrated ammonia and pour out excess of liquid. Cover jar with a glass plate. Place it over a jar of the HCl gas from the last experiment, bringing the jars mouth to mouth and remove plate. The ammonia unites with acid forming ammonium chloride, a salt.

Standing well away drop one or two small bits of sodium into a little distilled water in a bottle. When the action is over test the water with turmeric paper. The action of sodium on water gives sodium hydroxide, a base, and what gas? (see 13).

Test sodium hydroxide from shelf bottle with the papers. Pour about 5c.c. of the alkali into a dish and add dilute hydrochloric acid till the solution turns litmus paper red, testing by taking out a drop of the solution with a stirring rod and touching the paper; never place papers in the solution or dip them into it. Now add a few drops of NaOH or dilute HCl as may be necessary with stirring, till the solution changes neither turmeric nor blue litmus paper. It is now neutral. Evaporate to dryness, taste the residue. Place upon it a few drops of con. sulfuric acid and note odor of the gas. What was the solid residue?

**29.—**The preparation of HCl from salt and sulfuric acid gives a good example of a reversible reaction:



HCl is a stronger acid than  $\text{H}_2\text{SO}_4$ . In the cold or in a small closed space even on heating the reaction would not complete itself to the right. But, the HCl is easily volatile and heating drives it out of solution and away so that it cannot react with  $\text{HNaSO}_4$  to the left. Sulfuric acid is volatile only at very high temperature. Try restoring HCl thus: Dissolve with the least volume of water and heating, the contents of the flask used in preparing HCl. Cool some of the solution of  $\text{HNaSO}_4$  in a test tube and add a few c.c. of con. HCl from shelf, which will precipitate sodium chloride. Why is sulfuric acid used to prepare easily volatile acids from their salts? Why are the reactions completed when heat is used?

**30.—Preparation of Bleaching Powder, Potassium Hypochlorite and Potassium Chlorate:** Study these subjects in a text-book and read the experiment through.

Arrange the apparatus as shown in fig. 8. The wash bottle contains diluted sulfuric acid, made by adding 40c.c. of the con. acid with stirring, to 10c.c. of water. Its purpose is to remove the greater part of the HCl and water from the Cl. The horizontal test tube contains about 2 grams of dry slaked lime spread evenly throughout its



length. The upright test tube should contain a solution of 4 grams of potassium hydroxide dissolved in 12c.c. of water. It must be cooled and kept cold by surrounding with water as shown.

Charge the flask with  $\text{MnO}_2$  and diluted  $\text{HCl}$  as in 25. Maintain a moderate stream of chlorine for about 15 minutes or until the larger

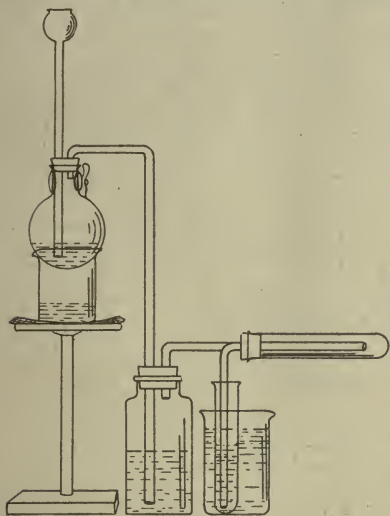


Fig. 8.

ing water through the filter several times, cool, let crystallize, pour off the water from the crystals, dissolve them in water and add silver nitrate. Compare the first and second precipitate formed by silver nitrate. Pure chlorate would give no precipitate.

Into a little of the hypochlorite solution place a drop of diluted ink, into another portion a bit of colored cloth. After noting any bleaching add a little dilute acid to each solution and note effect. To a third portion add a few drops of strong solution of ammonium hydroxide. What gas is given off?

Try the action of dilute acid on a little of the dry bleaching powder from the horizontal tube. Dissolve a portion of it so far as possible, filter and try the action of the filtrate on ink, colored cloth, litmus paper, before and after adding dilute acid.

To show the instability and oxidizing power of potassium chlorate mix on paper 5 grams of the salt and 5 grams of powdered sugar, but do not grind them together in a mortar. Place the mixture on an iron plate, take out a drop of con.  $\text{H}_2\text{SO}_4$  with the stirring rod, stand well away and drop the acid upon the mixture.

portion of it seems to pass through the solution in the second test tube. Now preserve half the contents of this tube as potassium hypochlorite, and heat the remainder to boiling and without cooling continue to pass chlorine into it for about five minutes or till a drop taken out with a stirring rod does not feel soapy to the fingers. Now heat to boiling and filter the solution. Cool by standing the tube in water, when crystals of  $\text{KClO}_3$  form. When quite cold filter them off and wash with a little cold water. Test the filtrate with silver nitrate. What was formed besides potassium chlorate? Dissolve the chlorate by passing about 3 cc. of boil-

## BROMINE AND IODINE.

**31.—Preparation of Bromine:** Place 5 grams of manganese dioxide and 5 grams of sodium bromide on paper, hold the neck of the retort pointing slightly upward and slide the mixture in at the tubulus without letting it fall into the neck of the retort. Support the retort as in fig. 9, add 50c.c. of dilute sulfuric acid through a funnel. The flask should contain about 100c.c. of water and the tip of the retort neck should dip under its surface. Apply heat and continue till all the bromine has distilled over. Move the flask away so as to bring the neck of the retort above the surface and then remove the burner. Is bromine soluble in water? Is it heavier than water? Set aside the

flask containing bromine for later use.

Give two reasons why we do not prepare Br in the same way as Cl; that is, by the action of hydrobromic acid on manganese dioxide?

May Cl be prepared by the same method used for Br; that is, by use of NaCl,  $\text{MnO}_2$  and diluted  $\text{H}_2\text{SO}_4$ ? Try it in a small way in a test tube, but strengthen the acid by adding about 1c.c. con.  $\text{H}_2\text{SO}_4$  to 2c.c. of dilute acid. Write equations for preparation of each.

Why is it not best to use con. sulfuric acid in preparing either

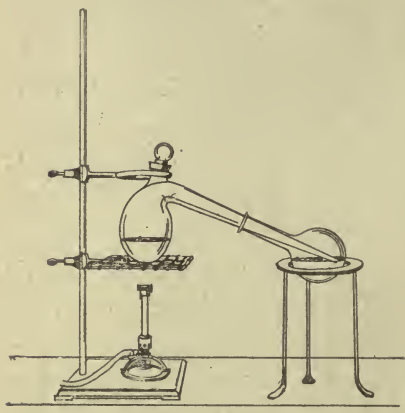


Fig. 9.

Br or Cl by this method?

**31.** By the same method prepare a little iodine, using about 0.5 gram of sodium iodide, a gram of  $\text{MnO}_2$  and 5c.c. of a mixture of dilute and con. sulfuric acid. Note sublimed iodine near the mouth of the test tube. Compare the reaction with that in the preparation of Cl and Br by the same method.

Heat a few crystals of iodine in a dry test tube. Does it form a liquid before subliming? What is sublimation? Note crystals higher up on walls of the tube.

**33.—Hydriodic Acid and Comparison of HCl, HBr, HI:** Treat very small amounts of sodium chloride, sodium bromide and sodium iodide with a few drops of con. sulfuric acid. How did you prepare HCl? Could HBr be prepared in the same way? What is the black substance set free by the action of the acid on sodium iodide?



When salt and sulfuric acid are heated together hydrochloric acid is set free, but no chlorine. Though  $\text{H}_2\text{SO}_4$  may be reduced and  $\text{HCl}$  oxidized, they are too stable to act on each other.

Though statements to the contrary are common, hydrobromic acid may be prepared in precisely the same way as you prepared  $\text{HCl}$ , remembering that the sulfuric acid there used was somewhat diluted. A very little  $\text{HBr}$  is oxidized by the  $\text{H}_2\text{SO}_4$  giving a trace of free bromine and sulfur dioxide. Write the equation. But when the gas is absorbed with water and the solution is distilled, the trace of  $\text{Br}$  quickly passes off, and the sulfur and its compounds that may be liberated are oxidized to sulfuric acid which remains to the last in the distilling vessel.

Hydriodic acid cannot be prepared by this method, since the  $\text{HI}$  is almost completely oxidized to free iodine and water, and the sulfuric acid is reduced to sulfurous acid and even to hydrogen sulfide.

Compare the degrees of stability of  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ , and compare these with their heats of formation by consulting a reference book.

**34.—Preparation of Hydriodic Acid:** Arrange a test tube as in fig. 10 high enough to permit heating and having a right angled delivery tube. Place in the dry test tube 5 grams powdered iodine and on top of it 0.5 red phosphorous, shake to mix, put tube in place and warm till the  $\text{P}$  and  $\text{I}$  react. When cool place delivery tube in small flask or bottle and by means of the pinch cock drop into test tube about 20 drops of water. Warm gently and collect the receiver full of  $\text{HI}$  and stopper it. Now place the delivery tube in water in test tube to absorb the gas, but have the tip of delivery tube just above the surface of the water.

Prepare a little  $\text{Cl}$  in a test tube by warming a few crystals of  $\text{KClO}_3$  and a little con.  $\text{HCl}$ . Pour some of the  $\text{Cl}$  into the flask containing the  $\text{HI}$ . What is set free?

Test the solution of  $\text{HI}$  in water with silver nitrate. What was the action of the  $\text{P}$  and  $\text{I}$ ? What was the action of this compound and the water? What is hydrolysis. Write all equations.

This same method with some modifications is often used for the preparation of hydrobromic acid. (See the text book for description.)

**35.—**Powder a few crystals of iodine in a mortar, place it in a test tube half full of water, and pass into the tube hydrogen sulfide gas prepared as in 68. Have the delivery tube reach quite to the bottom of the test tube. When all the iodine has disappeared boil the solution for a time to expel the excess of hydrogen sulfide and filter, several times if necessary to get rid of all the sulfur.

Test the filtrate with blue litmus paper. Set the solution aside to be used in the next experiment. Hydrogen sulfide here acts as a reducing agent. Write the equation.

**36.—Properties of Chlorine, Bromine, Iodine and Their Compounds:** Try to dissolve a little powdered iodine in water. Now pour off most of the water, add a few crystals of sodium iodide and shake. It is supposed the solution now contains  $\text{NaI}_3$ .

Try the solubility of I by pouring about 1 c.c. of carbon disulfide upon a crystal of I in a test tube and shaking. Now add water to the tube, shake and let carbon disulfide settle. In which liquid is most of the iodine? Try the solubility of iodine also in alcohol and in chloroform. Save the solutions of iodine.

Make a solution of starch by boiling about half a gram of starch in a dish or beaker half full of water and with stirring. Pour a little of the starch solution into a beaker of water, add a little iodine solution. This is a good test for free iodine. Add a little sodium iodide solution and a little of the starch solution to a beaker of water. To one portion add a little bromine water and to the other chlorine water. Is iodine set free by the Cl and the Br? To a solution of sodium bromide add chlorine water. Is bromine set free? To concentrate the bromine and also to show its solubility, to the liquid in the test tube add a little carbon disulfide, shake and let the latter settle.

Arrange the three halogens in the order of the ability of each to replace the others, and compare this order with that of the stability of their compounds with hydrogen.

To a little solution of iodine and to blue starch-iodine solution add a solution of sodium thiosulfate till the colors disappear.

To show the reducing power of hydriodic acid make very dilute solutions of potassium dichromate and potassium permanganate, add a little dilute sulfuric acid and then some of your solution of hydriodic acid. The chromate and permanganate are reduced and the solution is colored brown by iodine. For the same purpose treat a little of a solution of sodium iodate,  $\text{NaIO}_3$ , with dilute  $\text{H}_2\text{SO}_4$  and add some of your solution of HI. Refer to a text book and write the equations.

**37.—Tests for the Halogens:** How may each of the halogens in the free condition be recognized and tested for? (See 36). The following applies to them in the form of soluble halides:

To three tubes containing respectively a little dilute HCl or solution of any chloride, solution of any bromide, solution of any iodide, add a few drops of silver nitrate. Compare the colors of the three silver halides. Try to dissolve a little of each with ammonium thiosulfate. Try other portions with dilute nitric acid. Dissolve a

ammonium hydroxide. Try other portions with a solution of sodium little of each with potassium cyanide, KCN, being careful not to get it on the hands.

**38.—Hydrofluoric Acid:** Slowly and evenly heat a glass plate over a burner flame. Rub over the surface a piece of bees-wax so as to make a continuous film of the melted wax. When the wax has hardened, write on the plate with a pointed file or knife, cutting quite through the wax. In a lead dish place a little ammonium fluoride, or powdered calcium fluoride, moisten with con. sulfuric acid. Cover the dish with plate, wax side down, and apply a low heat to the dish so as not to melt the lead. After a few moments. remove the wax and examine the glass.

To test for a fluoride place a little of it mixed with a little sand, in a dry test tube, drop upon the mixture a little con.  $\text{H}_2\text{SO}_4$  and heat. While heating hold in the tube a wet stirring rod. Where wet the rod will be covered with a jelly-like layer of silicic acid. Why cannot a solution of  $\text{H}_2\text{F}_2$  be kept in a glass bottle?

### EQUIVALENT WEIGHTS.

**39.—Equivalent of Zinc:** Set up the apparatus as shown in fig. 10 and prove that all joints are tight by placing water in the funnel covering the end of the delivery tube with the wet finger and opening the pinch cock. The water should not run down. The end of the delivery tube should be bent upward and securely placed under the jar. Use pure, bright granulated zinc.

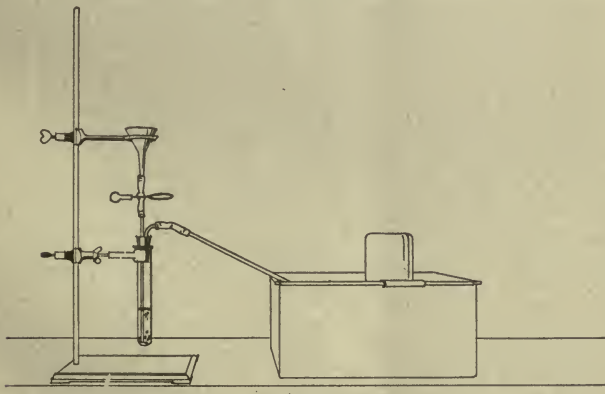


Fig. 10.

Weigh with great care not less than 0.2 grams nor more than 0.25 grams of the zinc for every 100c.c. that the jar or bottle will hold. If an analytical balance is used one weighing will suffice.

Horn pan balances are not very accurate and rarely in exact equilibrium. In this case weigh the zinc on one pan, then on the other and take half the sum of the weights. What errors in the balance will this practically eliminate? Place zinc in the test tube, fill collecting jar completely with water, and add 15c.c. of con. HCl to the funnel. Let in all the acid and close the clamp. When all the Zn is dissolved bring the level of the water in the jar to that in the trough and securely place on the cover. Dry the outside of the jar and weigh on the platform balance. Fill it completely with water and weigh again. The difference in grams less the volume of acid gives the volume of the hydrogen in cc. (V). Find the temperature of the water in the trough (t), and the reading of the barometer (P). Calculate the volume (V') to normal conditions by use of the formula,  $V' = V \times 273 \times (P - \text{aq. tens. at } t^\circ) \div (273 + t^\circ) \times 760$ . Why? The weight of H =  $V' \times .00009$ . The equivalent of zinc equals its weight divided by the weight of H  $\times 1.008$ , and its atomic weight equals twice this value.

**40.—Equivalents of Other Metals:** Find the equivalent of one or more of the following, using not more than the weights given for each 100 c.c. that the receiving vessel holds. Aluminium 0.07 gram; magnesium, 0.08; iron, 0.15. In the cases of aluminium and magnesium it is better to place the test tube in a beaker of water to keep the temperature down, and to use dilute acid. In the case of iron it may be necessary to warm the con. HCl used. Collect the hydrogen and proceed precisely as in the previous experiment.

**41.—Equivalent of Chlorine (a):** In normal times porcelain Gooch crucibles are cheap, and if they are available this method should be used; otherwise use (b).

Weigh accurately about 0.5 gram pure silver, preferably foil, place in a beaker, add 10c.c. water and 5c.c. pure nitric acid, and cover with clock glass. Warm if necessary, and after all is dissolved boil gently. Wash under side of glass and the inner surface of beaker till beaker contains about 75c.c. liquid, then add 20c.c. dilute hydrochloric acid and stir. Set in dark place till ready to filter. In a clean Gooch crucible make a mat of asbestos with aid of suction of the filtering pump as shown by the Instructor. It should be thick enough so that you cannot see light through it, dry for half an hour in oven at about 140 degrees, cool, in desiccator or on a clean surface and covered, twenty minutes and weigh.

With suction pump filter off silver chloride into crucible as shown, heat in oven one hour at about 140 degrees. Desiccate as before and weigh. Find weight of silver chloride and thence chlorine, and calculate the equivalent of chlorine if the equivalent of silver is 107.9.



The equivalents of bromine and iodine may be determined in the same way. Indirectly many other equivalents may be determined by the method as the following problem illustrates:

If 3 grams potassium chloride be treated with an excess of silver nitrate and the silver chloride weighs 5.773 grams, find the equivalent of potassium, if that of chlorine is 35.5.

(b) Weigh accurately a small porcelain dish, place in it about 0.5 gram of silver foil and weigh again. Add to dish 5c.c. con. nitric acid diluted with 10c.c. of water, cover with a watch glass. Give it time and do not heat unless necessary. When all the metal is dissolved, with a small amount of water in a fine stream from the wash bottle wash any spattered liquid from the under side of the watch glass, into the dish. Add to the dish 20c.c. pure dilute HCl and evaporate the liquid to complete dryness on a water bath. Heat the dish in an oven for half an hour at about 125°, or heat some distance above the burner flame till the silver chloride begins to melt. When fully cold weigh accurately the dish and contents, subtract from the weight of the silver chloride the weight of the silver and find the equivalent of chlorine calling that of silver 107.9.

**42.—Equivalents of Copper and Other Heavy Metals:** The equivalents of copper and several other metals may be determined by converting the weighed metal into nitrate with nitric acid, and decomposing the nitrate by heat, leaving the oxide.

Use accurately weighed copper foil or clean copper turnings, and proceed the same as in 41(b), but use no hydrochloric acid. Evaporate to complete dryness, and heat high over a flame with the watch glass on the dish. Gradually lower the dish and when nearly all blue color has disappeared, or all evidence of steam in the case of other metals, remove the watch glass and apply the full capacity of the burner for half an hour when there should remain a layer of black copper oxide. Material spattered upon the glass must be washed back into the cooled dish and the liquid must be evaporated again on the water bath, and the dish strongly heated. Weigh when quite cold.

From the weight of the copper oxide subtract the weight of the copper, and find the equivalent of copper calling oxygen 8. If 16 is used for oxygen the number obtained for copper is its atomic weight.

## NITROGEN AND ITS COMPOUNDS.

**43.—Preparation of Nitrogen From the Air:** Fill a pneumatic trough with water till it rises about  $\frac{1}{2}$  inch over the shelf. Place upon the shelf a small crucible or cupel and place in it as much red phosphorus as will lie on a half inch of the end of a knife blade or spatula. Ignite the P and at once place over the vessel and upon the shelf a jar or wide mouth bottle. Let the jar remain till it is cool and

the white fumes have been absorbed. Note the height to which the water has risen and estimate the ratio of the volume of oxygen which has been consumed to the nitrogen which remains. Slip cover on the jar, place it upright and test the gas remaining with a burning splinter. What other gases are mixed with the  $N$  thus obtained? Why does not this method give accurate results as to the volume of oxygen in air?

**44.—More Accurate Determination of Oxygen in Air:** Arrange the apparatus as shown in fig. 11. When all is adjusted, remove the test tube, mix about 7 cc. of a solution of pyrogallol with about the same volume of sodium hydroxide. At once pour the liquid into the funnel. By opening the clamp let the liquid down till it just reaches the lower end of the tube. Attach the test tube by inserting the stopper firmly, and opening the clamp move it till it closes out of the way upon the rubber and glass connecting tube. Move the test tube to a horizontal position to expose the air to more of the liquid surface. If the surface of the liquid in the funnel threatens to lower into the neck, add a little water. When you are sure the liquid has ceased to enter the test tube, invert the test tube and bring it up till the surfaces of the liquid in test tube and funnel are at the same height, as shown by the dotted lines. Estimate, or

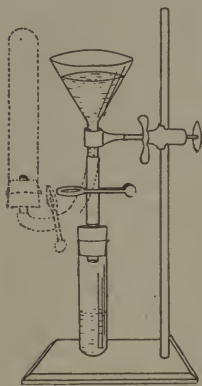


Fig. 11.

better, measure the lengths of the columns of the liquid in the test tube and the gas which remains. Which represents oxygen and which nitrogen? Find their ratio by volume in air.

**45.—Preparation of Nitrogen from Chemicals:** Set up the apparatus as shown in fig. 12. The nitrogen is obtained by heating a solution of ammonium nitrite but since this substance is difficult to make and to preserve, the same results may be obtained by heating a solution of ammonium chloride,  $NH_4Cl$ , and sodium nitrite,  $NaNO_2$ . These give in the solution the same groups,  $NH_4$  and  $NO_2$ , which form ammonium nitrite,  $NH_4NO_2$ .

Put in the flask 10 grams of ammonium chloride, 10 of sodium nitrite and 100c.c. of water. Heat and after the air has been expelled collect the nitrogen in jars.

Light a bit of candle, place it upon the deflagration spoon and lower it into a jar of the nitrogen. Lower burning phosphorus into another jar.

Note the curious fact in this experiment that the oxygen of ammonium nitrite oxidizes the hydrogen of the same compound; that is, one part of it acts as a reducing agent and the other as an oxidizing



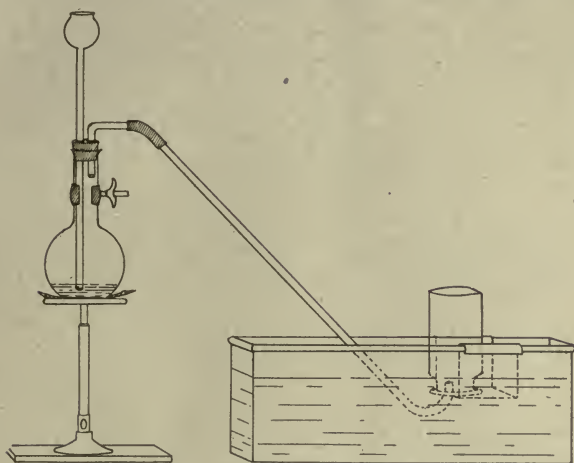


Fig. 12.

agent. Also, hereafter notice that whenever oxidation takes place with respect to one substance, reduction takes place at the same time with regard to some other substance. Find illustrations of this under preparation of chlorine, 24.

**46.**—An analogous method may be used for the preparation of N by heating an intimate mixture of ammonium chloride, 2 grams, and potassium dichromate, 5 grams, instead of ammonium dichromate. The method of heating and collecting is quite the same as that for oxygen in 6.

**47.—Preparation of Ammonia.** Place about a half gram of ammonium chloride, ammonium sulfate, ammonium nitrate in three test tubes. Add to each about 2c.c. of sodium hydroxide solution and warm. Note odor in each case, and hold in each tube a strip of moist turmeric paper. Repeat using about the same amounts of the ammonium compounds, but mix each with about its own weight of slaked lime. Formulate a general method of preparing ammonia.

Refer to a text-book for an account of calcium cyanamide, its manufacture, hydrolysis, use, importance. In a test tube place about a gram of the substance, barely moisten with water. Suspend in the tube a strip of moist turmeric paper, corking the tube and thus holding the strip in place. Observe evidence of ammonia after an hour.

Set up the apparatus as in fig. 13 and provide the dry fountain bottle as in 27. The collecting jars or bottles must be dry. Weigh and

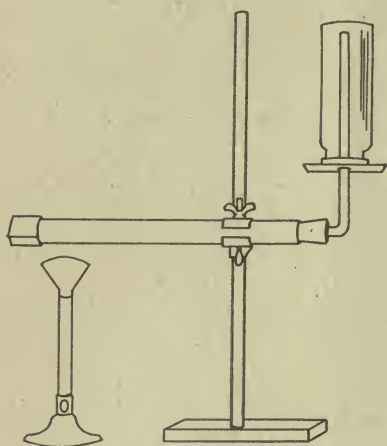


Fig. 13.

mix in mortar 10 grams each of ammonium chloride and slaked lime. Place on paper and slide into iron tube. Protect the stopper of tube with wet cotton. Heat the tube and collect two bottles or jars of gas by the downward displacement of air. When full moist turmeric paper held at the mouth of a jar will be instantly turned brown. While it is bottom upward clamp cover on jar or cover bottle with glass plate and place on desk bottom upward. Fill the fountain bottle and produce a fountain as with HCl in 27. Turn the delivery tube down

and place it in a test tube containing 10c.c. pure water so that the end of the delivery tube shall reach just under the water. Observe absorption of the ammonia and lower the delivery tube in the water as necessary to absorb all the gas. Heat as long as ammonia seems to come off, remove delivery tube from test tube then remove the lamp.

Observe odor of the solution of ammonia in the test tube. There is evidently gaseous ammonia above the liquid. There is also ammonia in solution, some ammonium hydroxide and some ionized ammonium hydroxide.

**48.—Action of Acids and Ammonia; Neutralization:** In a jar pour a few c.c. of con. HCl, wet the sides of the jar and pour out excess of liquid. Place over this the jar of ammonia gas, bottom upward, remove cover, placing jars mouth to mouth. Mix by reversing the pair, placing the jar with HCl above. The fumes and the solid on walls of jars consist of ammonium chloride,  $\text{NH}_4\text{Cl}$ , made by direct union of what? Try a burning splinter in the remaining bottle of ammonia gas.

In this paragraph and in all other such cases do not dip test papers into liquids, but take out a drop of the liquid with a stirring rod and touch it to the paper. In a porcelain dish place 10c.c. of ammonium hydroxide and neutralize with dilute nitric acid in just the same way as sodium hydroxide was neutralized with HCl in 28. Evaporate about two-thirds of the liquid over a flame and complete the evaporation on a water bath. Why on a water bath? Press dry the ammonium nitrate between folds of filter paper.

Small quantities of ammonia may be tested for as directed in Qualitative Analysis, Group V. Very small quantities are tested for

with Nessler solution, which is a strongly alkaline solution of mercury and potassium iodides. If at hand and to show the sensitiveness of the test, fill a clean test tube nearly full of distilled water, and in another tube of distilled water dissolve a granule of ammonium chloride as large as a pin head. To each tube add about 2c.c. of Nessler solution. In very dilute solutions the amounts of ammonia are in proportion to the depths of color, and the test is much used to determine very small amounts of ammonia in water.

**49.—Preparation of Nitrogen Monoxide (Nitrous Oxide):** Set up the apparatus as in fig. 12, but omit the thistle tube. Heat in the dry flask 15 grams of ammonium nitrate, and regulate the heat so as to control the flow of gas, which should be collected in three jars or bottles. When through collecting remove the delivery tube from the water, then remove the burner.

In one jar thrust a glowing splinter. In another lower burning phosphorus. Burn a piece of picture cord in the same way as in oxygen. Write the equation and compare it with the self-oxidation of ammonium nitrite to form nitrogen.

**50.—Preparation of Nitric Acid:** Arrange the retort and receiving flask as in the preparation of bromine, fig. 9, but retort and flask should preferably be dry. Put into the retort as there described 20 grams of sodium or potassium nitrate. Add through the tubulus of the retort by means of a funnel 25c.c. of con. sulfuric acid. At once wash the funnel and measuring cylinder. Let stand till acid and solid are in contact throughout and then heat with a small flame, preferably of the crown top. There is no need of cooling the receiving flask if the heat applied is properly regulated. Turn down the flame if fumes escape in considerable amount from the flask. Stop heating when the acid comes over slowly and the liquid in the retort is clear and seems to be viscid. What is the substance left in the retort? To remove it when cool fill the retort nearly full of water and heat gently, best on a water bath. Pour off solution, add fresh water and heat again. Repeat till all is dissolved. If the cake of solid comes loose do not shake it about, since the thin retort will be broken.

**51.—Oxidizing Action of Nitric Acid:** Nitric acid, after free oxygen, is the most important of all oxidizing agents and its oxidizing action should be well understood.

When the very concentrated acid is heated a part of it breaks down thus:  $(1) 2\text{HNO}_3 = \text{H}_2\text{O} + 2\text{NO}_2 + \text{O}$ . Whenever the more dilute acid is in contact with something easily oxidized the reaction is likely to be:  $(2) 2\text{HNO}_3 = \text{H}_2\text{O} + 2\text{NO} + 3\text{O}$ . To illustrate, (a) heat a few drops of your acid and note the red-brown gas given off. (b) Place a loose plug of woolen yarn in the mouth of a test tube which contains about 2c.c. of your acid, and boil the acid till the vapors set the wool on fire. (c)

Heat a little sawdust in a dish till it begins to char and pour upon it about 1 c.c. of your acid. (d) Place about 3 grams of sugar in a flask and 25 c.c. of con. nitric acid from the shelf. Heat till copious fumes of  $\text{NO}_2$  are formed. The sugar is mainly oxidized to oxalic acid. The next experiment contains a good illustration of oxidation of metals by  $\text{HNO}_3$ .

In the most common case of oxidation with nitric acid the acid itself is reduced to water and nitric oxide,  $\text{NO}$ . Oxidation and reduction, it will be remembered, go on together usually. In some cases the reduction does not go so far. An instance is the reduction of a nitrate to nitrite by heating with lead (see 54). In some cases the reduction proceeds to the formation of hydroxyl-amine,  $\text{HONH}_2$ , but more often to ammonia. To illustrate this treat a few bits of aluminum in a test tube with about 3 c.c. of sodium hydroxide, and add 2 drops of con. nitric acid. Warm the tube and when the action becomes rapid note odor of ammonia. Incline the tube and hold in it moistened turmeric paper without touching the glass. Here the hydrogen from the sodium hydroxide and Al reduces the nitric acid to ammonia. Arrange in a horizontal line in note book the successive reduction products of nitric acid.

**Aqua regia** is a mixture of 1 part of con. nitric with 3 parts of con. hydrochloric acid. Make about 1 cc. of the mixture, heat it and notice chlorine given off. It will dissolve many substances that are attacked by neither of the acids alone.

**52.—Action of Nitric Acid on Metals, Nitric Oxide:** See in a text book the electro-motive series, and the action of nitric acid on metals.

The very electro-positive metals will give some hydrogen with dilute nitric acid. Set up the apparatus to prepare H, but use a test tube instead of the flask. Place in tube magnesium turnings. Dilute con.  $\text{HNO}_3$  by mixing 5 c.c. with 30 c.c. of water. Fill two test tubes with water and have them ready to collect the gas. Put in the dilute acid, about 5 c.c. at a time and after the air has been expelled collect two test tubes of the gas. Test the gas for H. Note red gas in test tube when air enters, using the second tube. Save the liquid in the tube in which H was evolved. Repeat the experiment, using granulated zinc instead of magnesium. Can you detect any H? Note red fumes of nitrogen dioxide,  $\text{NO}_2$ , always formed when nitric oxide,  $\text{NO}$ , comes in contact with air or oxygen. When the action is over pour off a little liquid from the Zn and test it and the solution saved from the magnesium for ammonia: To the liquid add NaOH in excess, hold a strip of moist turmeric paper in the tube not letting it touch the glass and warm gently. Also note odor of ammonia.

The metals lower than zinc in the electro-motive series give no H with nitric acid, and those below hydrogen do not give H with any



acid. Try the action of con. nitric acid diluted with an equal volume of water, on a little tin, copper, powdered antimony. Oxides are obtained with the first and third metals. Would HCl act on the copper and antimony? Could  $\text{HNO}_3$  and metals be used to prepare pure H?

**53.—Nitric Oxide:** Use apparatus as in fig. 3. Put in flask 25 grams granulated copper, about 10 cc. water, see that thistle tube reaches into the water, then add con. nitric acid as necessary to secure a moderate flow of gas. Reject the first half jar full of gas. Fill three jars, leaving one on the shelf of the trough. Pass some of the gas through a solution of ferrous sulfate in a tube. The dark color is due to  $\text{FeSO}_4\text{NO}$ . What does the blue solution in the flask contain? Pour it into a vessel provided for the purpose. Wash the remaining copper and put into the vessel provided for it.

Prepare oxygen as in 6 or 9 and pass a little into jar on shelf. The red gas is nitrogen dioxide,  $\text{NO}_2$ . Let it become absorbed then pass in more oxygen. Thus continue till the water ceases to rise in the jar. Write the volume equation for the union of NO and  $\text{O}_2$ . What is formed when  $\text{NO}_2$  dissolves in cold water; in hot water?

In one jar of NO burn red phosphorus. Try a candle in the other.

Express the action of nitric acid on copper in two equations, the first of which shows the decomposition of the acid in oxidation as in equation (2), 51, forming  $3\text{CuO}$ ; the second the dissolving of this oxide in the acid.

**54.—Reduction of a Nitrate to Nitrite, Nitrous Acid:** (a) In an iron crucible heat and stir with an iron rod, spike nail, 5 grams of potassium nitrate and 20 grams granulated lead till the mass glows. When cold add water and boil for some time. Filter off the liquid into a tube. Add an excess of dil.  $\text{H}_2\text{SO}_4$ . Test the gas with moist starch iodide paper. The sulfuric acid sets free nitrous acid which breaks up into water, NO and  $\text{NO}_2$ ; equations. Note that  $\text{NO} + \text{NO}_2 = \text{N}_2\text{O}_3$ , the anhydride of nitrous acid. It exists only as a liquid.

(b) Read (a) carefully. In a flask with thistle tube and right-angled delivery tube place 10-grams sodium nitrite, add enough water to cover end of thistle tube, place delivery tube in 5 cc. NaOH in a wide test tube. Add about 25 c.c. dil. sulfuric acid to the flask. Nitrous acid is set free, but breaks up as in (a). The gases are absorbed by the NaOH making  $\text{NaNO}_2$ . Add dilute acid to this solution and test the gas as in (a).

**55.—Nitrogen Dioxide, Nitrogen Tetroxide:** The lead nitrate used in this experiment should be prepared in quantity before the laboratory period by crushing to moderate fineness in a mortar and heating for three hours in an oven at about  $125^\circ$ .

Heat 10 grams of the dried lead nitrate in iron tube shown in fig. 13, turning the delivery tube down, and placing it in a small dry flask.

Heat until the flask is filled with the red-brown gas,  $\text{NO}_2$  mixed with  $\text{N}_2\text{O}_4$ . Stopper the flask and heat it high over a flame, but do not heat so much as to burst the flask. A temperature of  $142^\circ$  is sufficient to change all the gas to  $\text{NO}_2$ . Note depth of color. Let the flask cool a few moments in air, then under running water, and observe the depth of color again, when 80% of the gas will consist of colorless  $\text{N}_2\text{O}_4$ . Write the equation for the production of the gas and the reversible reaction of the change from one to the other constituent of the mixture.

Heating lead nitrate again pass the gas into about 3 cc. of sodium hydroxide for a few moments, then add dilute sulfuric acid to the solution. What evidence have you that a nitrite was formed by the action of the gas on sodium hydroxide? What else was formed? See text book for the action of this gas with cold water and with hot water.

**56.—Tests for Nitrogen and the Nitrate Radical:** (a) Tests for nitrogen in organic matter: Heat in a test tube with soda-lime or a mixture of lime and powdered sodium hydroxide, bits of woolen material, such as yarn, or bits of leather, dry albumin or corn meal, and hold in the mouth of the tube wet turmeric paper. Is ammonia given off?

Secure an imperfect test tube and heat in it any of the organic substances mentioned, with a bit of sodium not larger than half a pea. (Do not touch sodium with the wet hands). Heat strongly till the reaction is complete, and standing well back place the hot end of tube in a little water in a beaker. The end cracks off. Boil the water and filter. To a portion of the filtrate add a little solid ferrous sulfate, then a few drops of ferric chloride, and boil. Now make acid with dilute  $\text{HCl}$ , when a deep blue color will result. To the rest of the solution add a crystal of potassium nitro-ferri-cyanide, which will give a red color, showing sulfur in the organic matter.

(b) Tests for the nitrate radical, or nitric acid: To a few cc. of a solution of ferrous sulfate add a very little of any nitrate, and when the substance is dissolved and the solution is cool incline the tube and pour in steadily con.  $\text{H}_2\text{SO}_4$ , so that it will run down and collect at the bottom of the tube. Where it and the solution meet will form a dark ring of  $\text{FeSO}_4(\text{NO})$ .

The following test should be used only for excessively small amounts of nitrate: Upon a bulk of any nitrate not larger than a pin head and in a dish, drop about ten drops of phenol-disulphonic acid. Warm the dish gently, best on a water bath for a few moments. Add about 25 cc. of water and make alkaline with ammonia. A yellow solution shows nitrate radical is present.

## ELECTRO-CHEMISTRY—THEORY OF IONIZATION.

**57.—Electrical Terms and Fundamental Laws:** Using good text books on chemistry and on physics study, till clear to you, the meaning

of these terms: anode, cathode, Volt, Ampere, Ohm, Coulomb, Watt, electro-chemical equivalent, electro-motive series of the elements.

What is Ohm's Law? On a 110-Volt circuit find the current strength or amperage transmitted by a 25-Watt lamp. Find the resistance of this lamp in Ohms.

What is Faraday's Law? What are the electro-chemical equivalents of H, O, Cl, SO<sub>4</sub>, NO<sub>3</sub>, Cu, Ag, Sn'', Sn'''? Give relations of electro-chemical equivalents, atomic weights (or in the case of radicals the sum of the atomic weights), and valences.

**58.—Electrical Conductivity:** The current used is the direct lighting circuit, 110 volts, cut down by a 25-Watt lamp. This would give what amperage through a wire without resistance connecting the two binding posts? Calculate and read the ammeter. Do the results agree?

Determine the comparative conductivity of the following 5th normal solutions, already made by the instructor: hydrochloric acid, sulfuric acid, acetic acid, sodium acetate, sodium hydroxide and ammonium hydroxide. Since they are all N/5, they have the same number of chemical equivalents per unit volume. According to whose law might they be expected to conduct the same?

To determine the conductivity secure one of the conductivity tubes

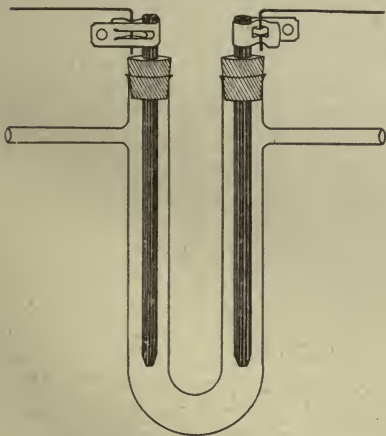


Fig. 14.

as shown in fig. 14, wash, rinse with distilled water and drain it. In each case be careful thus to clean the tube. Paste a strip of gummed paper on it and in each case fill to this mark. Connect the tube thus filled with the binding posts, note the intensity of the glow of the lamp and read the ammeter. Thus determine the conductivity of all. Why should they conduct so differently? \*Knowing the resistance of the lamp and the current it alone transmits, calculate from one of your readings of the ammeter the resistance of the solution?

Fill the conductivity tube with a neutral solution of sodium or potassium sulfate, add a few drops of litmus solution and mix well, and subject the solution to the action of the current. Which electrode gives off oxygen and shows the formation of acid around it; which shows hydrogen evolved and alkali formed around it? Try a solution of common salt without litmus solution. Prove with starch-iodide pa-

per that Cl is given off at the anode. Test the solution at the cathode with turmeric paper. By what secondary reaction is alkali formed in the last two instances? What is the action of sodium on water? (13)

In electrolysis many of the heavy metals instead of acting upon water at the cathode are there deposited. Subject a solution of copper sulfate to electrolysis for several minutes. What is deposited on the cathode? What gas is given off at the anode? Copper sulfate itself reacts slightly acid, but if the solution at the anode be tested it will be found much more acid. How do hydrogen and the metals accumulate at the cathode and the acid radicals, with which they were associated, at the anode?

**59.—Chemical Facts Best Explained on the Theory of Ionization:**  
**The Nature of Acids:** Test with blue litmus paper dilute HCl, dilute  $\text{HNO}_3$ , dilute  $\text{H}_2\text{SO}_4$ , acetic acid and any other acids that may be available. Why should substances of such different composition all turn the paper red? Why should they all taste sour? Try the action of each on bits of zinc. Why should all give hydrogen? Why should they all neutralize bases giving salts and water? Why should they all give hydrogen at the cathode when electrolyzed?

It would seem that H is the one component of all acids, and that to it their acid properties are due. In electrolysis H accumulates at the cathode and the rest of the acid molecule at the anode. It is not far to the thought that the H is, in the solution of an acid, comparatively free from the rest of the molecule. Since unlike electric charges attract each other and like charges repel, the inference is that the H atom is charged positively thus,  $\text{H}^+$ , and the remainder of the molecule, for example Cl is charged negatively, thus,  $\text{Cl}^-$ . In this condition the H and Cl atoms are called ions. Ions are formed when acids, bases and salts are dissolved in water and without regard to any influence of the electric current.

**60.—The Character of Bases:** Test with turmeric paper solutions of sodium hydroxide, potassium hydroxide, ammonium hydroxide, calcium hydroxide, barium hydroxide. Again, why should such different substances all turn the paper brown? They also all neutralize acids in the same way forming salts and water. Their common constituent is hydroxyl OH. Since all bases have OH it is inferred that the alkalinity is due to this group. It seems to be easily separable from the metal or such group as  $\text{NH}_4$ . In electrolysis it travels to the anode where it breaks up into water and oxygen while the metal goes to the cathode. For reasons given under acids, it is believed that a base in solution is more or less ionized. That is, sodium hydroxide consists largely of the ions  $\text{Na}^+$  and  $\text{OH}^-$ .

**61.—Ready Cleavage or Ionization of Salts:** In as many test tubes place a few drops of solutions of the following:  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{CaCl}_2$ .



$\text{BaCl}_2$  and other chlorides that may be at hand. Add to each a few drops of silver nitrate. Why should all these different chlorides give the same precipitate of silver chloride? Silver sulfate or silver acetate might have been used instead of silver nitrate and precisely the same precipitate of silver chloride would have resulted. In the solutions of chlorides it is evident that chlorine is very slightly held by the metals if at all, and the same is true of the silver in the solutions of the silver salts. All these salts are electrolytes, the metals going to the cathode and the non-metals to the anode. The inference is that they are largely ionized in solution. Thus, sodium chloride is largely  $\text{Na}^+$  and  $\text{Cl}^-$ , and silver nitrate is  $\text{Ag}^+$  and  $\text{NO}_3^-$ .

Any element as Cl is not always an ion in solution. To solutions of pure potassium chlorate, chloral and chloroacetic acid add a little silver nitrate solution. No silver chloride is obtained, since  $\text{KClO}_3$  ionizes into  $\text{K}^+$  and  $\text{ClO}_3^-$ , chloroacetic acid into  $\text{H}^+$  and  $\text{CH}_2\text{ClCO}_2^-$ , while chloral hydrate gives no ions.

**62.—Degree of Ionization:** Refer to your experiment on conductivity (58). Did all the acids conduct equally well and were they equally ionized? Compare the conductivity and ionization of sodium hydroxide and ammonium hydroxide; of acetic acid and sodium acetate.

The ionization of the same substance may be increased by diluting and decreased by concentrating its solution.

(a) Compare the colors of 2-normal solutions of copper sulfate, nitrate and chloride. The color of each is supposed to be due to the color of the undissociated salt and to the copper ion. Now dilute a small portion of each solution with 10 times its volume of water. Why are the solutions now more nearly the same color? To a portion of each solution add an excess of ammonia. The same color is due to the same ion,  $\text{Cu}(\text{NH}_3)_4^{++}$ .

(b) The concentration of a solution may be in effect increased and the dissociation of the solute decreased by adding a substance having an ion in common with the solute. Solid copper bromide is black, its concentrated solution is brown due to  $\text{CuBr}_2$ , while its dilute solution as that of every other cupric salt shows blue due to the Cu ion. In a dish dilute about 2 c.c. of the brown solution till it becomes blue. To one half of the blue solution add a few drops of con.  $\text{HBr}$ , which has the common ion  $\text{Br}^-$ , till brown. To the other half add solid copper chloride, having the common ion  $\text{Cu}^{++}$ , till brown. Explain how the addition of the common ion effects these changes.

(c) Dilute a little acetic acid from shelf bottle with 20 times its volume of water. Add a few drops of methyl orange and divide into two portions. To one add one half its volume of con. sodium acetate and compare its color with that of the other half. What common ion was added and what was the effect on the acidity of the acid?

(d) To a saturated solution of salt add concentrated HCl till a large precipitate of salt is obtained, and account for its formation.

**63.—Acidity Due to Hydrolysis:** Many substances containing no hydrogen give an acid solution. They are mostly salts of metals which form weak bases and radicals of stronger acids. With blue litmus paper test solutions of salts of copper, iron, aluminium. In these cases the hydrolysis goes only a little way, for example thus:



Add a little antimony chloride and bismuth chloride to five times their volumes of water. Here the reactions go far to the right precipitating  $\text{SbOCl}$  and  $\text{BiOCl}$ . Now reverse the reactions by adding con. HCl. See the hydrolysis of the halides of phosphorous, 34 and 79.

**64.—Alkalinity Due to Hydrolysis:** Some salts of strongly basic metals and weak acids give alkaline solutions due to hydrolysis. Test with turmeric paper or a few drops of phenol-phthalein solutions of borax, sodium carbonate,  $\text{Na}_2\text{CO}_3$ , and sodium phosphate,  $\text{HNa}_2\text{PO}_4$ . In the case of sodium carbonate,  $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} = \text{HNaCO}_3 + \text{NaOH}$ , and of course the last is highly ionized, and the alkalinity is due to the ion  $\text{OH}^-$ . For other examples see 77 and 95.

**65.—The Electro-Motive Series of Elements:** In the following any metal which replaces another from solution is said to have a greater solution tension or to be more electro-positive. In a little zinc sulfate solution place bits of magnesium turnings and let stand. When the action has nearly ceased note gray deposit of zinc. Place zinc in a solution of cadmium chloride and later note cadmium deposited on the remaining zinc. Try cadmium or zinc in solutions of copper sulfate and lead acetate and note copper and lead deposited. Try iron in a copper solution. Place a strip of copper in a solution of mercuric chloride and after a few minutes remove, rub and note mercury coating. Put a copper wire in a silver solution and note deposit of silver. Try silver in a solution of gold chloride and note deposit of gold on the silver. All these cases are practically alike. One metal goes into solution as ions and the other is as it were forced out as neutral metal; for example,  $\text{Cu}^{++} + \text{SO}_4^{--} + \text{Zn} = (\text{reversibly}) \text{Zn}^{++} + \text{SO}_4^{--} + \text{Cu}$ . Write a similar ionic equation for the preparation of H with zinc and sulfuric acid. Has the  $\text{SO}_4$  much to do with either case?

Arrange the above metals in the order of their capacities to replace other metals, or their ionizing tendency. Compare the result with the arrangement of the Electro-Motive Series in a text-book. What two metals above if used for the plates in an electric battery cell would give the greatest electromotive force?

## SULFUR.

**66.—Solubility and Crystallization:** Do not heat carbon disulfide or have a flame near it, since it is very volatile and easily inflammable.

Place in a dry test tube about 2 grams of powdered sulfur, add not more than one-fourth test tube full of carbon disulfide, shake and filter through a dry filter into a crystallizing dish or small beaker. Let two or three drops fall into a clean watch glass. After the liquid has evaporated at room temperature, examine the crystals in each vessel, and those in the watch glass with a microscope. The crystals belong to the rhombic variety of sulfur.

**67.—Effects of Heat, Allotropic Forms:** Since the test tube cannot be cleaned fill an imperfect one three-fourths full of lumps of sulfur, slowly and evenly heat till it is all changed to a yellow, mobile liquid. Now increase the temperature and note that it becomes darker. Find a temperature at which the tube may be inverted for a moment without the sulfur's running out. Increase the temperature till it shows signs of boiling and becomes quite fluid again. Pour in a steady small stream into a beaker or other vessel full of water. Examine this "plastic sulfur", place aside and examine at the end of the laboratory period and at the next period. It gradually changes to monoclinic sulfur, and after a long time to rhombic, the permanent form. Consult text-book on the forms of sulfur, and their properties.

**68.—Hydrogen Sulfide:** Fit a small bottle or flask, the former preferred, with a delivery tube consisting of two right angled pieces joined with rubber tubing, the outer piece long enough to reach to the bottom of the collecting vessel or test tube when resting on the desk. Place in the generating vessel 20 grams of ferrous sulfide in small bits, sliding in the larger pieces to avoid breakage if a flask is used, add about 40 c.c. of water and drop directly upon it a little at a time con. sulfuric till a suitable flow of gas is secured. If the flow of gas becomes too slow at any time do not add more acid, but pour off the liquid which is nearly exhausted of acid but contains much iron salt, and add water and acid as in the beginning.

Collect a bottle of the gas by displacement of air, in the same way as chlorine, and burn the gas in the bottle. What is the deposit on the sides of the bottle? Collect gas in a test-tube one-fourth full of water, cover mouth of tube with the thumb and shake. Is the gas soluble in water? Turn upward the outer section of the delivery tube and light the gas at the orifice. Hold cold porcelain as a dish or crucible lid in the flame at about its middle. What is the yellow deposit? Insert the flame into a bottle with wide mouth as far as you can with-



out extinguishing the flame. Why does sulfur deposit on the dish and bottle instead of burning?

**69.—Precipitation with Hydrogen Sulfide:** Hydrogen sulfide is much used in separating the metals into groups in analytical chemistry. In test tubes in the test tube holder place about 5 c.c. of solutions of salts of the following metals, using chlorides, nitrates, acetates as may be convenient: silver, lead, mercury, bismuth, copper, cadmium, antimony, arsenic, tin; also, zinc, cobalt, nickel, manganese, iron; also, barium, calcium, strontium, sodium, add a drop or two of dilute HCl or  $\text{HNO}_3$  to each. Pass the gas flowing with moderate rapidity into each of these solutions for about a minute, washing off the delivery tube by dipping into water before inserting it into a new solution. Note carefully what metals can be precipitated as sulfides with  $\text{H}_2\text{S}$  from slightly acid solutions remembering the acid added and the fact that when precipitation occurs acid is necessarily set free. The precipitation of zinc is not complete. Pass an excess of gas into the tube containing zinc, filter off the precipitate and add to the filtrate and to each succeeding solution, beginning with cobalt, ammonium hydroxide, which should give precipitates of sulfides in all until barium is reached. That is, several metals not precipitated as sulfides in acid solution are precipitated with hydrogen sulfide and an alkali and they form another group. Name the metals not precipitated as sulfides.

Return to the sulfides precipitated from acid solution, pour off the liquid from the sulfides of Hg, Cu, Bi and try to dissolve each by boiling with dilute nitric acid. How may Hg be separated from the other two? Pour off the liquid from the sulfides of lead, antimony and arsenic and heat each with about 5 c.c. of ammonium sulfide, but do not boil. How may lead sulfide be separated from arsenic and antimony sulfides?

These are merely illustrations of the use of hydrogen sulfide and many others will be met. Instead of using hydrogen sulfide and ammonium hydroxide separately to precipitate certain sulfides, it is common practice to use ammonium sulfide which may be easily made by saturating diluted ammonium hydroxide solution with hydrogen sulfide, and then adding an equal volume of the same ammonia solution which gives essentially  $(\text{NH}_4)_2\text{S}$ .

**70.—Reducing Action of Hydrogen Sulfide.** Hydrogen sulfide is not a very stable compound and it acts as a reducing agent in much the same way as hydriodic acid. Pass hydrogen sulfide into a dilute acidified solution of potassium dichromate, till green; into a dilute acidified solution of potassium permanganate till colorless; into bromine water and a dilute solution of iodine till colorless. In the last two cases filter off the sulfur and test liquids with litmus paper. What



acids were formed? Compare the reducing action of hydrogen sulfide with that of sulfur dioxide in experiment 71.

**71.—Sulfur Dioxide:** (Read reference book on sulfur dioxide, sulfur trioxide and sulfuric acid.) In a test tube treat a little sodium sulfite with dilute acid. Note odor and test with a strip of paper moistened with mercurous nitrate. It should turn dark.

Determine whether bits of charcoal and sulfur will give  $\text{SO}_2$  when heated with con. sulfuric acid. Explain their action on the acid. Arrange apparatus as in the preparation of hydrochloric acid. Place in the flask 20 grams of granulated copper or bits of sheet copper or turnings and add 25 c.c. con. sulfuric acid. Before heating read through the experiment and have everything needed at hand so as to continue the flow of gas the minimum of time.

Heat till gas comes off freely and control the rate by turning down the flame. After acidifying them with acetic acid pass gas into a solution of potassium dichromate till green and into a solution of potassium permanganate till colorless; also, into bromine water till colorless, into dilute nitric acid, and into distilled water. To each solution add barium nitrate and then dilute  $\text{HCl}$ . The formation of a white precipitate by barium nitrate, insoluble in  $\text{HCl}$  shows the presence of the sulfate radical,  $\text{SO}_4$ .

The first action of  $\text{SO}_2$  on passing it into the above solutions was probably the formation of the unstable sulfurous acid,  $\text{H}_2\text{SO}_3$ . All the substances into which the gas was passed were oxidizing agents except of course the distilled water. Show their action on the sulfurous acid. Test for the sulfate radical in the dilute sulfuric acid on the shelf, in solutions of magnesium sulfate, copper sulfate and other sulfates that may be at hand.

**72.—Preparation of Sulfuric Acid:** Set up the apparatus as shown in fig. 15. The ignition tube may be of hard glass or of half inch gas pipe. If the latter is used it should be 12 to 14 inches long to prevent the overheating of the stoppers. Even then it is well to spray the ends with the wash bottle catching the water as it runs off, or to wrap the ends with cotton or filter paper and keep it saturated with water.

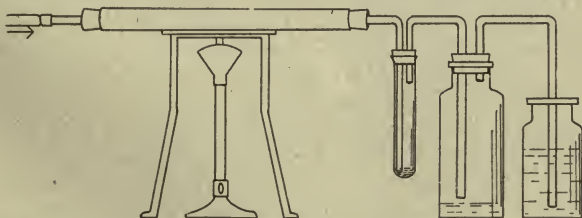


Fig. 15.

Using loose plugs of asbestos fiber or steel wool confine near the middle of the tube about 15 grams of granular iron pyrite. Connect the outer end of the tube with the compressed air system. If this is not available a bulb pump, foot-bellows or even a bicycle pump may be used to force through the air. Instead of forcing through the air the other end of the apparatus may be connected with the exhaust system or a filtering pump.

Place in the test tube 3 c.c. of con. nitric acid, preferably fuming acid, and to the larger bottle, connected with it add about 5 c.c. of water. The smaller bottle contains a solution of sodium hydroxide to absorb the excess of noxious gases.

Heat the tube containing the pyrite, preferably with a wing burner and force or draw through a moderate stream of air. When the bottles are filled with white fumes it may be known that the pyrite is oxidizing. Moderate the heat to avoid distilling off unburned sulfur, and regulate the air so that only a small amount of fumes escape from the smaller bottle. Continue the operation 10 to 20 minutes. To avoid sucking back remove the air connection and then the burner.

Transfer the liquids in the test tube and larger bottle to a weighed porcelain dish, rinse with a little water and add this to the dish. With a free flame evaporate till the steam and nitric acid vapor give place to the dense gray fumes of sulfuric acid. Let the dish cool and weigh it. Three to four grams of con. acid should be made in a 10 minutes run. Show that the acid will carbonize a splinter dipped into it. Dilute a few drops of it and test with barium chloride. Remove and examine the contents of the ignition tube. What results from burning iron pyrite in air?

**73.—Sodium Sulfite and Thiosulfate:** Dissolve 10 grams anhydrous sodium carbonate in 50 c.c. of water with aid of heat if necessary, cool and place just one half of the volume in a large test tube. Pass into the solution in tube sulfur dioxide made by heating in a flask with thistle tube 25 grams of copper turnings with 25 cc. of concentrated sulfuric acid. The delivery tube should reach to the bottom of the test tube. When the flow of gas begins the heat should be reduced so as to avoid a too rapid stream. As the carbon dioxide is set free the liquid shows a tendency to froth. The reaction is completed in about 15 minutes when small bubbles disappear, the sulfur dioxide apparently is no longer absorbed, and the liquid smells strongly of the gas. The result is acid sodium sulfite. Now add this solution to the reserved half of the sodium carbonate solution which will give normal sodium sulfite. Why? Place the combined solutions in a dish and boil for two or three minutes. If evaporated nearly to dryness on a water bath and allowed to cool crystals of sodium sulfite would be obtained. The whole of the salt may, however, be converted into sodium thiosul-

fate. For this purpose add to the solution three grams of powdered sulfur and boil gently for twenty minutes replacing from time to time the water evaporated. Filter off the sulfur and evaporate the filtrate over a water bath till crystals begin to form and let the solution become cold.

Pour off the solution from the crystals and use it to study the properties of sodium thiosulfate.

To a small volume of a solution of iodine add the solution of thiosulfate till the iodine solution is decolorized.

Make a little silver chloride by adding a few drops of a solution of some chloride to a few drops of silver nitrate. Now add the thiosulfate solution, a little at a time with shaking, till the silver chloride dissolves. What is the use of sodium thiosulfate, "hypo," in photography?

To the remainder of the solution of thiosulfate add an excess of dilute hydrochloric acid, warm and note the precipitation of sulfur and the odor of sulfur dioxide. Account for the gas and the sulfur.

Here as elsewhere study the experiment with aid of a reference book till all is clear and write the equations.

## PHOSPHORUS.

**76: White and Red Phosphorus, Allotropic Forms:** (Caution: Handle white phosphorus only with the forceps. Keep trace of all pieces used and any remaining must not be left about the laboratory desk or thrown in waste jars, but put into a vessel of water provided for that purpose).

Place a piece of white phosphorus as large as a grain of wheat in water in a test tube and boil. Phosphorus vapor goes off with the water vapor but burns to oxide on reaching the air. Try red phosphorus in the same way. Does it volatilize?

Heat a little red P in a dry narrow test tube and note sublimate of white P on wall of tube. Change white P to red P by dropping a small crystal of iodine upon white P in a dry test tube and warming.

Dissolve a little white P in about 3 c.c. of carbon disulfide in a dry test tube, pour the liquid upon filter paper, place this upon the ring of a retort stand and let dry. Try to dissolve red P in a little carbon disulfide. Do not have a flame near carbon disulfide. What is meant by "allotropic forms"?

**77.—Phosphine:** Drop a piece of fresh calcium phosphide into a small bottle or beaker full of water. The gas set free is mainly phosphine,  $\text{PH}_3$ , but it is mixed with another hydride,  $\text{P}_2\text{H}_4$ , which takes fire spontaneously.

**78.—**(Caution: The following experiment is a beautiful one, but it is attended with some danger. It may be undertaken by a small

class under constant supervision). Set up apparatus as in the preparation of nitrogen, but place the end of delivery tube in a dish of water, fig. 12. Place in the flask about 20 cc. of sodium hydroxide, made by dissolving the solid in three times its weight of water. Add two or three small bits of white P, then about 1 c.c. of ether having no flame near, stopper the flask and heat. When the gas begins to ignite on reaching the air, moderate the heat so as to maintain a rate of one bubble every two or three seconds. Carefully insert the delivery tube into a test tube of alcohol by which the  $P_2H_4$  is dissolved. Does the escaping gas now take fire?

When cold carefully remove the stopper, fill flask with water, wash the remaining P and place in vessel of water provided.

**79.—Chlorides of Phosphorus and Hydrolysis.** Refer to 34, 63. In a dish place one drop of water and add one drop of phosphorus trichloride, best from a dropping bottle. What acid gas is given off? What acid of P remains? In another dish place about the same amount of water and phosphorus pentachloride of about the bulk of a pea, handling it with the spatula. What gas is here given off? Save the liquid to test for phosphoric acid in the next experiment.

**80.—Tests for the Radical  $PO_4$  and Phosphoric Acids:** (a) To a few c.c. of sodium phosphate add one-fourth its volume of ammonium chloride, make alkaline with ammonia and then add magnesium sulfate. The slowly forming precipitate is ammonium magnesium phosphate,  $(NH_4) Mg PO_4$ , and this is a good test for phosphoric acid provided arsenic acid is not present. Add water to the second dish in the preceding experiment, boil, transfer to a test tube and test for  $PO_4$ .

(b) To test for phosphate in a substance insoluble in water dissolve a small portion in dilute nitric acid, and to a few drops of the solution add twice its volume of ammonium molybdate and warm. A yellow precipitate shows phosphate, provided arsenic acid is known to be absent. If practicable secure a piece of bone, place it in dilute nitric acid, and near the end of the period test the solution for phosphate by this method.

(c) To solutions of sodium phosphate  $HNa_2 PO_4$  and "microcosmic salt,  $NH_4HNaPO_4$ , add silver nitrate. Note color of precipitate the same in both cases and try its solubility by adding to one tube dilute nitric acid and to the other an excess of ammonia.

**81.—Other Acids of Phosphorus:** In a crucible heat a small amount of ordinary solid sodium phosphate and after the water of crystallization has been driven off continue with full flame for five



minutes. When cold dissolve some of the fused mass and test with silver nitrate. The ordinary sodium phosphate,  $\text{Na}_2\text{HPO}_4$ , has been changed to sodium pyrophosphate,  $\text{Na}_4\text{P}_2\text{O}_7$ . Repeat this experiment using microcosmic salt. While the water is evaporating test for ammonia with turmeric paper, and note odor. This salt is changed by heating to sodium metaphosphate,  $\text{NaPO}_3$ , at high temperature. Let the crucible cool, dissolve most of the metaphosphate and test with silver nitrate. Compare the silver tests for phosphate, pyrophosphate and meta-phosphate.

### ARSENIC.

82.—Acidify strongly with dilute  $\text{HCl}$ , dilute solutions of sodium arsenite  $\text{Na}_3\text{AsO}_3$  and arsenate  $\text{Na}_3\text{AsO}_4$ , and without heating pass into each  $\text{H}_2\text{S}$ , for a few moments. Do you get a precipitate in the second solution? Now heat each nearly to boiling and pass in the gas again till the precipitation is complete. Filter off the arsenic sulfide,  $\text{As}_2\text{S}_3$ , and wash it on the filter. Try to dissolve a part of the substance in con.  $\text{HCl}$  in a dish. Now, boiling only gently add very small bits of potassium chlorate from time to time till nearly all the sulfide is dissolved. Add a little more con.  $\text{HCl}$  to replace that boiled away, if necessary. Make alkaline with ammonia the solution in the dish and filter, and to the filtrate add a solution of magnesium sulfate or chloride. Compare this test for arsenate with that in the next section, and with the test for phosphoric acid. (80a.)

Remove most of the remaining sulfide to a clean dish, add about 5 c.c. of ammonium sulfide and heat but do not boil. This is a method of separating arsenic sulfide from many other sulfides. To the solution add an excess of dilute  $\text{HCl}$  which will reprecipitate the arsenic sulfide together with some sulfur.

83.—Treat dilute solutions of sodium arsenite and arsenate with silver nitrate and note carefully the colors of the precipitates. Try the solubility of portions of each with dilute nitric acid and with ammonia. Treat a solution of the sodium arsenate with ammonium chloride, make alkaline with ammonia and add a solution of a magnesium salt. Compare the precipitate with that obtained in (82) in the same way and also under phosphoric acid. How may an arsenate be distinguished from a phosphate? Given a mixture of arsenate and phosphate how could you remove the  $\text{AsO}_4$  and test for the  $\text{PO}_4$ ?

84.—Tests for Small Amounts of Arsenic: One of the following may be used:

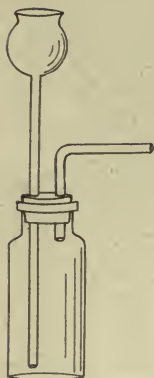


Fig. 16.

(a) **The Modified Gutzeit Test:** Good filter paper should be wet with a solution of mercuric chloride, allowed to dry, and cut into strips narrow enough to slip into the horizontal tube, fig. 16. An arsenic solution containing 0.01 mg. per c.c. and another containing 1 mg. per c.c. is made up for class use. On no account should ordinary arsenic solutions be used in this or the next, (b).

Place a strip of the paper in the tube, and about 10 grams of coarsely granulated zinc in the bottle, and add 15 c.c. of dilute HCl with an equal volume of water. After a little time look to see whether the paper shows by brownish color that the materials used contain arsenic, and if not add 5 c.c. of the arsenic solution of 0.01 mg. of arsenic. Let stand 20 minutes and observe color of paper.

(b) Set up apparatus as in fig. 17, the outer section of delivery tube being of hard glass. Place in flask 10 grams pure zinc and add pure dilute sulfuric acid.

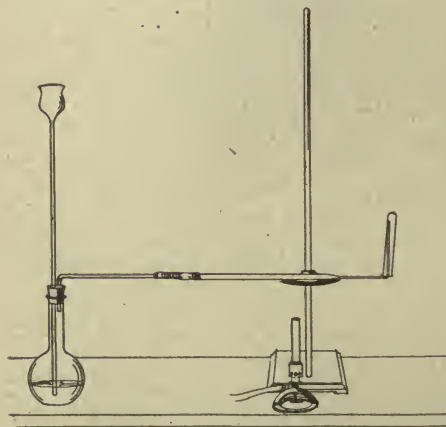


Fig. 17.

When air is expelled light the gas with a test tube. Now heat the tube and add 5 c.c. of the solution marked .01 mg of arsenic to 1 c.c. After several minutes examine arsenic mirror beyond the heated portion. Move flame toward mirror. Is the latter easily volatilized? Now remove lamp and add to flask 5 c.c. of the solution marked 1 mg. of arsenic to 1 c.c. Hold in the flame a porcelain evaporating dish or crucible lid. Examine the spots of arsenic formed,

and try the action of a solution of sodium hypochlorite upon them. Antimony also gives a similar mirror and spots, but it is not soluble in the hypochlorite.

85.—If desired to use either of the tests for arsenic for practical purposes, prepare five standard papers or five standard tubes containing .01, .02, .03, .04 .05, mg. of arsenic by using 1, 2, 3, 4 and 5 c.c. of the solution containing .01 mg to 1 c.c.

Now cut a piece of highly-colored wall-paper for example, one decimeter square, tear into bits, place in a dish, heat with 5 c.c. con. sulfuric acid, until the paper is completely charred. Let cool, treat contents of dish with 25 c.c. of water, stir well and filter. Test the solution for As as above, using only so much as necessary to obtain a mirror or paper containing .01 to .05 mg. of arsenic. Compare with standards, and calculate the amounts of As to one sq. meter of wall paper. A similar proceeding will suffice for cotton fabric.

### ANTIMONY.

86.—Heat about 0.5 gram of finely powdered antimony with about 10 c.c. con. HCl. Does it dissolve? Now add to the test tube about 1 c.c. of con. HNO<sub>3</sub>, being careful that the liquid does not froth over on the hand. When most of the metal is dissolved pour a little of the solution into test tube of water, and another portion into a solution of salt. Compare the precipitate of antimony oxy-chloride SbOCl in the two tubes, allowing for salt which may precipitate in the second tube and quickly settle. Add con. HCl to the first tube till the precipitate just dissolves, and pass an excess of H<sub>2</sub>S into the two solutions. Also pass the gas into solutions of tin chloride and bismuth chloride. Filter off the precipitated antimony sulfide and wash on filter. Remove a little of the precipitate Sb<sub>2</sub>S<sub>3</sub> to a dish and boil with a little con. HCl. How may antimony be separated from arsenic? See 82.

Dissolve a portion of the sulfides of antimony and tin by warming in a dish with yellow ammonium sulfide, and try to dissolve bismuth sulfide in the same way. To the solutions of Sb and Sn sulfides add an excess of dilute HCl when the sulfides will be reprecipitated. How may antimony, arsenic and tin in solution be separated from bismuth and most other heavy metals?

To illustrate the separation of antimony and tin dissolve their sulfides together in hot con. HCl, boil for a few moments, dilute the solution with twice its volume of water, put in "card teeth" or steel wool and boil persistently. Filter off the black scales of Sb and to the filtrate add a solution of mercuric chloride. A white precipitate of mercurous chloride shows stannous chloride, SnCl<sub>2</sub>, was present. Dissolve the black scales on the filter with a very little aqua regia, dilute with 20 times its volume of water and pass in H<sub>2</sub>S which will precipitate antimony sulfide.

### CARBON.

87.—In a test-tube held in a clamp with its mouth slightly lower than the other end, heat a block of wood. Light the gas given off and let any liquid distilled fall into a vessel not worth cleaning. Examine

liquid and test for acid. When the volatile products cease to come off examine the charcoal left in tube as to its form, structure, lightness.

In a small flask boil solutions of litmus, cochineal, and indigo with powdered bone charcoal and filter. Use about 3 g. fresh charcoal with 25 c.c. of each solution. If any one of the filtrates is not clear return it to the flask, boil again and filter.

**90.—Preparation of Carbon Dioxide:** Provide a bottle or flask with thistle tube and two-piece delivery tube as in 68. Put in 25-50 grams of calcium carbonate, cover it and the tip of thistle tube with water, and add a little con. HCl from time to time to maintain a moderate flow of  $\text{CO}_2$ . Three or four jars of gas may be collected in the same way as chlorine.

Now pass the gas into a test tube half full of clear lime water till the precipitate of normal calcium carbonate,  $\text{CaCO}_3$ , formed at first completely dissolves as it is changed into the acid carbonate,  $\text{H}_2\text{Ca}(\text{CO}_3)_2$ . Reverse the reaction by boiling one half of the solution. To the other half add lime water which will precipitate the normal carbonate. (See 116).

Pass  $\text{CO}_2$  into 5 c.c. 3-normal sodium hydroxide, slowly enough to make absorption apparent.  $\text{Na}_2\text{CO}_3$  is formed at first, but later the acid carbonate,  $\text{HNaCO}_3$ , which being sparingly soluble, is precipitated. Reverse the reaction to the  $\text{Na}_2\text{CO}_3$  by boiling. Test a few drops of the solution and also small amounts of other carbonates for carbon dioxide thus: Place a little of the carbonate in one test tube and a few c.c. clear lime water in a larger one. Add an excess of dil. HCl to the carbonate and pour the gas set free, but no liquid, into the lime water, shielding the mouths of the tubes from air currents as shown in lecture room. A white precipitate in the lime water shows carbon dioxide and a carbonate.

**91.—**Introduce into a jar of carbon dioxide rapidly burning phosphorus. Place a bit of burning candle in a beaker and pour carbon dioxide upon it from a jar. Which is more dense,  $\text{CO}_2$  or air?

Determine whether a candle will burn in the exhaled breath by filling the lungs to capacity, exhaling through a tube into a jar, and without delay lowering into it a bit of burning candle.

**92.—**Carbon dioxide may be prepared by heating acid sodium carbonate, "soda," or magnesite,  $\text{MgCO}_3$ , as in Fig. 13 but turning the delivery tube downward. Soda decomposes into the normal carbonate so easily that a test tube may be used. For magnesite the iron tube is better. In this case the reaction is similar to that in making lime by heating  $\text{CaCO}_3$ .

**93.—(a) Carbon Monoxide:** Set up the apparatus as in Fig 18, having the bottles two-thirds full of NaOH, one part of the solid to three of water. Place in flask 20 grams oxalic acid and 40 c.c. con.



$\text{H}_2\text{SO}_4$ . Prepare a tube with copper oxide as in Fig 5, if (b) is assigned.

Heat the flask so as to maintain a stream of gas slow enough to permit the absorption in the bottles of the  $\text{CO}_2$  which comes off with the  $\text{CO}$ .

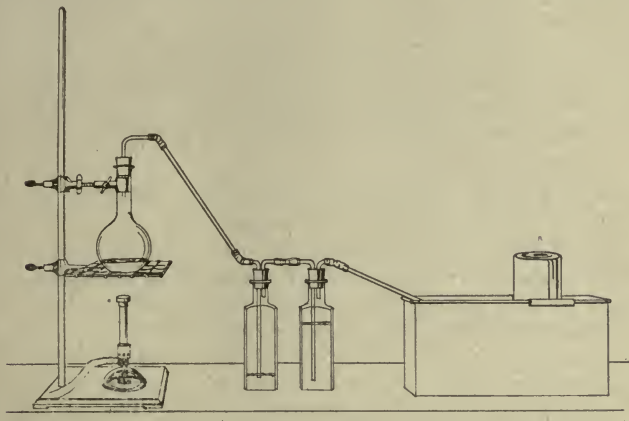


Fig. 18.

After a jar full of gas has come over, place delivery tube in a test-tube of lime water. It should not become turbid. If turbid, decrease the rate of flow. Collect two jars full of gas. Remove cover of one jar, quickly pour in lime water, seal and shake. Burn the gas in the jar and shake again. Apply a flame to the mouth of the other jar, add lime water, seal and shake. What is formed by burning  $\text{CO}$ ?

Disconnect flask from bottles and place its delivery tube in a test-tube of lime water. What other gas is mixed with the carbon monoxide? To determine the amount of this gas fill a slender test-tube with the mixture by displacement of air, slowly withdraw the delivery tube and cover mouth of test tube with the wet finger. Place mouth of tube under sodium hydroxide in porcelain dish and let it remain until the volume of gas no longer decreases. Estimate the volume of remaining gas as compared with the original volume of the mixture and test it with a flame.

(b) Disconnect the delivery tube and substitute for it the tube prepared with copper oxide. Support this tube on a ring, connect with a test tube of lime water. Heat the copper oxide and pass over it a slow stream of carbon monoxide. Use more oxalic acid in the generating flask if necessary. Is the copper oxide reduced? What is formed by its action on carbon monoxide? For the great importance of this pro-

perty of carbon monoxide see the chemistry of the blast furnace in the text book.

**94.—Methane, Marsh Gas:** Mix intimately in a mortar 10 grams of fused sodium acetate  $\text{CH}_3\text{CO}_2\text{Na}$  and 10 grams of soda lime. Place in a retort of gas pipe, provided with a two-piece delivery tube and heat as in the preparation of oxygen, collecting two jars of gas. Light the gas and study the degree of luminosity of the flame. Hold the flame under the mouth of a dry bottle or jar and note appearance of moisture. Put lime water in the jar and shake. Pass the gas through lime water in a test tube. What evidence have you that methane contains hydrogen and carbon?

To the other jar of  $\text{CH}_4$  add a little bromine water and shake. Does methane absorb bromine?

**95.—Acetylene:** Cuprous chloride is required, and should be freshly prepared as in 126. For the preparation of acetylene fit up the apparatus in Fig. 10, but substitute a small flask for the test tube. Place in flask about 10 grams of calcium carbide, and by means of the funnel and clamp let in upon the carbide water, a few drops at a time. When the air has been expelled as shown by collecting and burning a test tube of the acetylene, collect three bottles of the gas. Insert the delivery tube into a solution of cuprous chloride made alkaline with ammonium hydroxide. The red precipitate is cuprous acetylide,  $\text{Cu}_2\text{C}_2$ . In the same way precipitate silver acetylide from a solution of silver nitrate made alkaline with ammonia. These acetylides are explosive and should be washed into the sink before they become dry.

Insert the delivery tube into a test tube half full of bromine water and let the gas run for several minutes. Also, shake in one of the bottles a little bromine water with acetylene. Compare its action on bromine to that of methane.

Uncover one bottle of gas, wait a moment, then apply a flame. Why is there a bright flash followed by quiet combustion giving a very smoky flame?

**96.—Flame.** Regulate a Bunsen burner so as to produce a small slightly luminous flame. Observe the three parts, lower and inner portion which is non-luminous, luminous portion, outer non-luminous portion. Compare with a candle flame. With a short piece of glass tubing draw off gas from lower part of flame and burn it at the end of the tube. Try the same with candle flame. Hold a piece of wire gauze in candle flame just above the wick and observe interior. Can you light unburned gas above the gauze? Hold a piece of paper for an instant in the same position and examine under surface. Repeat experiments with gauze and paper using the flame of a Bunsen burner. Also turn on gas, hold gauze close to the burner tube and light gas above gauze. Now move gauze to one side.

**97.—Oxidizing and Reducing Flames.** Regulate a burner so as to produce a small luminous flame, and find by trial the best position for tip of blowpipe to produce a long slender blowpipe flame with well-marked inner blue reducing and the outer non-luminous, oxidizing portions.

Make a cavity with butt of pliers or a small coin in a piece of charcoal, place in it a small quantity of lead oxide and heat in the reducing flame of the blowpipe. Continue until a globule of lead remains. Caution: After using charcoal with the blowpipe always extinguish any fire by holding it under the faucet and then return it to the charcoal tray.

**98.—Fermentation of Glucose.** In a 500 cc. flask dissolve 25 grams of glucose, 1 gram each of sodium-potassium tartrate, ammonium nitrate and sodic phosphate in about 250 cc. of hydrant water. Rub with a little water in a mortar one-tenth of a cake of yeast and wash into flask. Connect the flask with a gas washing bottle nearly full of clear lime water, set in a warm place and let remain three or four days. Observe from time to time the carbon dioxide given off. Take out a drop of the liquid, place on a slide, cover and examine for cells of the yeast plant with a microscope.

Arrange the flask as in fig. 6 and distill off 20 c.c. keeping distillate well cooled. Clean the flask, put in the 20 c.c. and distill off about 5 c.c. Test this second distillate for alcohol, first testing for it in a known solution as follows: to about 5 c.c. water add about 1 c.c. alcohol and a few crystals of iodine, and shake. Warm the tube and add gradually a solution of sodium carbonate till the iodine disappears. Iodoform will appear, at any rate on cooling. Let a few drops cool on a watch glass and examine with the low power of a microscope. Now examine for alcohol the distillate above.

**99.—Reducing Power of Sugars. Invert Sugar.** Fehling's solution is a mixture of equal volumes of two solutions, one containing 34.639 grams of copper sulfate to 500 c.c. and the other 173 grams sodium potassium tartrate and 60 grams sodium hydroxide in 500 c.c. The copper in 1 c.c. of the mixture is reduced by 0.005 gram of glucose.

To about 10 cc. Fehling's solution add enough glucose to precipitate all the copper on boiling as cuprous oxide,  $\text{Cu}_2\text{O}$ , which will settle, leaving the clear liquid above. In a fresh mixture try a little milk sugar. Try cane sugar.

Now dissolve about a gram of cane sugar in 100 c.c. of water, add a few drops of con. HCl, heat to 70 degrees and let cool. Boil 10 c.c. of this solution of invert sugar with 20 c.c. of Fehling's solution.

**100.—Esters, Acetic Ester:** Acids act upon alcohols forming esters and water much as they act upon bases forming salts

and water. Acetic acid and alcohol act thus:  $\text{CH}_3\text{CO}_2\text{H} + \text{C}_2\text{H}_5\text{OH} = \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 + \text{H}_2\text{O}$ .

Use the apparatus shown in Fig. 6. With the delivery tube in the test tube pour into test tube 20 c.c. water and mark the level with gummed paper. Remove the water. Place in the flask 15 c.c. glacial acetic acid, 15 c.c. alcohol and 5 c.c. con. sulfuric acid. Warm the flask with a very small flame so that only a few drops shall distill over in 10 minutes. Now increase the heat and distill to the 20 c.c. mark. Instead of measuring the distillate a two hole stopper and thermometer may be used, and the distillation continued till it reads  $95^\circ$ . Its bulb should be in the vapor above the liquid.

The ester contains acetic acid and alcohol. To remove most of these shake it persistently with twice its volume of water in a small flask covered with the thumb. On standing the ester rises and forms the top layer. Separate it from the water by using a separatory funnel, or the funnel with pinch cock and exit tube as shown in Fig. 10. Measure the purified ester.

In a test tube shake about 2 c.c. of your ester with an excess of NaOH till it all disappears; that is, till it is all "saponified" forming sodium acetate and alcohol.

Note odor of acetic ester. Upon this is based a good test for acetic acid or its salts. To a little solid sodium acetate in a test tube add a few drops of alcohol and a few of con. sulfuric acid and note odor. Another test is this: To a neutral solution of an acetate add 3 drops of ferric chloride. A red color should be obtained, and on boiling a brown flocculent precipitate.

**101.—Saponification, Soap Making:** In a dish or beaker place five grams of olive oil or lard or tallow, add 15 c.c. of alcohol and 5 c.c. of sodium hydroxide solution of concentration one to four. Do not use a pipette for NaOH. With occasional stirring heat on a water or steam bath, for at least half an hour, but better, an hour. All the alcohol and most of the water should be evaporated. Examine the soap when cold. If the saponification is complete a small portion should entirely dissolve in water, save a slight milkiness. Dissolve more of the soap and determine whether it will form a lather with soft water. Try blowing soap bubbles with the solution. Determine whether the feeling is that given by ordinary soap.

Filter some of the soap solution. Pour a little into distilled water, into hydrant water, into solutions of calcium and magnesium sulfates. Shake each tube and determine in which ones a persistent lather is formed. To those in which it is not formed add more soap solution and shake again, until a lather persists. Calcium and magnesium compounds make water "hard." Why do such waters require more soap?



To a concentrated solution of soap add dilute hydrochloric acid in excess. The precipitate consists of a mixture of organic acids of which stearic acid,  $C_{17}H_{35}COOH$ , is representative. The oils and fats mentioned above consist of mixtures of what are known as esters of these acids. The most common perhaps is stearin,  $(C_{17}H_{35}COO)_3C_3H_5$ . Write the equation for the saponification of stearin with sodium hydroxide; also, write equation for action of soap on solution of calcium sulfate.

### SILICON.

**102.—Silicic Acid.** To 10 c.c. of a solution of sodium silicate in a small beaker add con. HCl drop by drop stirring for a few moments after each addition. Silicic acid will separate as a jelly. Collect the silicic acid on a filter, wash with water, transfer to a crucible, dry over flame and finally ignite. When cold try to dissolve the residue in water, in hydrochloric acid.

**103.—Boric Acid:** Place 15 g. borax in 50 c.c. water in a beaker. Heat till dissolved and add 15 c.c. con. HCl with stirring and allow the liquid to cool thoroughly. Filter off and examine the boric acid. Dissolve a little of the substance in alcohol in a dish, set fire to alcohol and observe color of the flame. Moisten a strip of turmeric paper with the solution from the boric acid. Observe color, then treat the paper with a solution of sodium carbonate, let dry, best on steam bath, and note color.

### QUALITATIVE TESTS FOR THE COMMON ACIDS

**106.**—The substance given for analysis may be in solution. If not, dissolve in water, heating if needed. If not soluble in hot water use dilute nitric acid, and heat. If gas is given off one or more acids of group (1) are present, and the special tests may be applied at once.

**Group (1):** To a small portion of the solution add dilute  $HNO_3$  in excess if not already added, and heat. If gas is set free try to identify it by odor, color and tests. Only  $CO_2$ ,  $SO_2$ ,  $H_2S$ ,  $NO_2$  are likely to occur. Make special tests for the following acids as given in the sections indicated by the numbers:  $H_2CO_3$  (90),  $H_2SO_3$  (71),  $H_2S_2O_3$  (73),  $H_2S$  (68),  $HNO_2$  (54b).

**Group (2):** To another portion of the solution add dilute nitric acid in excess if not already present and if members of group (1) are present boil to expel any gas. To a portion of the boiled solution add barium chloride in excess. A white precipitate shows  $H_2SO_4$  (71). Filter it off and make filtrate alkaline with ammonia. A yellow precipitate indicates  $H_2CrO_4$  (140). A white precipitate indicates one or more of the following:  $H_3PO_4$  (80),  $H_3AsO_4$  (83),  $H_3AsO_3$  (83),  $H_3BO_3$  (103),  $HF$  (38),  $H_2C_2O_4$  (see following): To another portion of

the boiled solution add ammonia in excess, then  $\text{CaCl}_2$ . An immediate precipitate may mean any of the acids of this group save sulfuric. Add an excess of acetic acid. If the precipitate is insoluble, oxalic acid or hydrofluoric or both are present. To a third portion of the boiled solution add manganese dioxide, which will give  $\text{CO}_2$  if oxalic acid is present. It is well in any case to make the special test for boric acid, since its barium and calcium salts are distinctly soluble.

**Group (3)** To the original solution add silver nitrate. If a precipitate is formed add an excess of dilute nitric acid. If the precipitate all dissolves this indicates some acid in previous groups. If insoluble, one or more of the following are present:  $\text{HCl}$  (37),  $\text{HBr}$  (37),  $\text{HI}$  (37),  $\text{H}_2\text{Fe}(\text{CN})_6$  (142),  $\text{H}_3\text{Fe}(\text{CN})_6$  (142). A pure white precipitate shows only  $\text{HCl}$ . If the precipitate is colored proceed to the special tests for the others. For halogen acids see also 127b.

**Group (4)** Nitric and acetic acids must always be tested for if the substance is soluble in water. For  $\text{HNO}_3$  see (56b), and for acetic, (100).

### SODIUM, POTASSIUM, LITHIUM.

107.—Through a spectroscope suitably adjusted by the instructor examine a flame colored by a sodium salt, and locate the sodium line on the scale. Locate in the same way the red line given by potassium, and that given by lithium. Draw a millimeter scale in your note book and place the lines in their correct positions. If the spectroscope has no scale, estimate as closely as possible the relative positions of the three lines. Note that any chemical will show some sodium. Its line is no evidence that sodium is present in considerable quantity.

108.—What is the action of sodium on water? Standing well back drop a bit of potassium into water in a bottle or beaker. How does the result differ from that given by  $\text{Na}$ ?

To reduce the violence of the action of the alkali metals on water their alloys with some other metal are often used. Drop into water "hydrone" which is an alloy of sodium and lead. Also try sodium amalgam, an alloy of sodium and mercury. When the action of the latter is over put the mercury in a dish provided for the purpose. Never put mercury into sinks. Why? Test the solution in each case with red litmus or turmeric paper. Test soapy feeling of the solution between thumb and finger.

109.—**Preparation of Sodium Hydroxide:** Dissolve 5 grams of sodium carbonate in 75 c.c. of water in a porcelain dish and reserve 5 c.c. Heat the remainder nearly to boiling, and stir in a little at a time 5 grams of slaked lime. Boil gently for several minutes, replacing the water evaporated, let settle and filter off the solution. If it destroys the filter, let cool, add a little water and use another filter. To prove

the reaction,  $\text{Na}_2\text{CO}_3 + \text{Ca}(\text{OH})_2 = \text{CaCO}_3 + 2\text{NaOH}$ , proceed as follows: Wash the insoluble residue in the dish twice by filling nearly full of water, stirring, letting the substance settle and pouring off the water. Now put a little water on the insoluble substance in dish, and place about the same amounts of lime and water in another dish and pour upon each about 10 c.c. of dilute HCl. Compare the amounts of carbon dioxide given off. Now treat the 5 c.c. reserved solution of sodium carbonate and the same volume of the filtrate with the same volumes of HCl and compare the gas given off. You started with a soluble carbonate and a very sparingly soluble hydroxide, "slaked lime." What did you obtain by the reaction?

**110. Comparative Tests of Crude and Pure Sodium Hydroxides:** Dissolve 1-2 grams of crude and pure NaOH, each in 10 c.c. of distilled water. Make each acid throughout with dilute nitric acid and warm. If either gives off gas test for carbon dioxide as in 90. Test small portions of each acidified solution for Cl with silver nitrate, and other portions for  $\text{SO}_4$  with  $\text{BaCl}_2$ . Test other portions for iron by adding to each a few drops of potassium ferrocyanide and potassium ferricyanide, which will give a blue color if iron is present.

**111.—Purification of Common Salt:** If practicable use the crude rock salt of the feed store, but ordinary salt will do. Dissolve about 5 grams in 25 c.c. of water. To one third add dilute HCl and test for  $\text{SO}_4$ , and preserve the tube and contents. To another portion add a little ammonium chloride, make alkaline with ammonium hydroxide and add ammonium carbonate. The precipitate is calcium carbonate. Filter it off and to the filtrate add sodium phosphate which will give a precipitate on standing if magnesium is present. See 80. Save this tube and contents.

Make a fully saturated solution of the crude salt, first reducing it to powder if rock salt is used, and shaking a long time with water. Filter if necessary and to the solution add an equal volume of pure con. HCl. This will precipitate most of the salt. If gaseous HCl were added more salt would precipitate. Filter off the salt and wash with three small portions of water. Dissolve some of this salt in water, test for  $\text{SO}_4$ , calcium, magnesium, as above and compare with the results of these tests with crude salt.

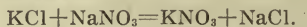
**112.—An Acid Salt, Acid Potassium Tartrate, Cream of Tartar:** This is one of the few slightly soluble salts of potassium. As the term is commonly used there are no insoluble salts of Na or K. Dissolve about 4 grams of pure, dry potassium carbonate in 25 c.c. of water and 10 grams of tartaric acid in 50 c.c. of water, measuring the latter solution. To the carbonate solution add one drop of methyl orange, then add cautiously the acid solution till a faint red color is obtained. This gives the soluble normal salt,  $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$ . Note what volume of the acid



solution was added, then add as much more, stir and let stand some time. The precipitate is the acid tartrate, cream of tartar. Which salt is least soluble?

Filter off the cream of tartar, let it dry on the filter and weigh with a balanced filter. Calculate the weight of acid sodium carbonate to mix with it to make one kind of baking powder which when wet acts thus:  $\text{HKC}_4\text{H}_4\text{O}_6 + \text{HNaCO}_3 = \text{NaKC}_4\text{H}_4\text{O}_6 + \text{H}_2\text{O} + \text{CO}_2$ . What makes the bread rise when baking powder is used? Try your baking powder in a tube with water and test for  $\text{CO}_2$ .

**113.—Potassium Nitrate from Sodium Nitrate:** Dissolve in 50 c.c.  $\text{H}_2\text{O}$ , 25 g. sodium nitrate and the calculated amount of potassium chloride required in the reaction



Evaporate to one-half the volume, let the separated salt settle, and decant the clear, hot liquid into a beaker, press solid with spatula and let liquid run into beaker. This solution should turn solid when cold. Transfer this to a filter and let drain. Press solid between folds of filter paper, dissolve in least hot water and let crystallize. Transfer crystals to filter and let dry.

**114.—Qualitative Analysis:** Determine first the presence of the ammonium radical and the alkali metals in known substances, and then their presence or absence in "unknowns," using the scheme as given 152, Group V. In the initial work fresh substances will be examined, and of course what is said of filtrates from previous groups and their preparation for analysis does not apply.

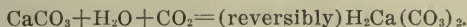
### BARIUM, STRONTIUM, CALCIUM, (MAGNESIUM).

**115.**—Upon a piece of quick lime drop water as long as it is taken up, place it in a dish and observe from time to time. After it has become powdery place some of the "slaked" lime in a jar of water, shake it thoroughly and let settle. Filter a portion of the nearly clear lime water placing the funnel in a flask to protect from the carbon dioxide of the air. Test the clear solution with turmeric paper. To portions of the lime water add one-third of their volumes of ferric chloride and magnesium chloride respectively. The precipitates are hydroxides of the metals. Test the alkalinity of barium hydroxide and its action on solutions of the same metals.

**116.**—Pass carbon dioxide into 25 c.c. of clear lime water until the precipitate of calcium carbonate,  $\text{CaCO}_3$ , dissolves, forming the acid carbonate,  $\text{H}_2\text{Ca}(\text{CO}_3)_2$ . The latter is the chief substance that gives "temporary hard water." To a small portion of the solution add clear lime water. How may lime soften temporary hard water? Will lime also remove magnesium from water? Boil another portion of the so-



lution which will reverse to the left the reaction which occurred with  $\text{CO}_2$  in excess.



**117.—Pure Calcium Chloride:** Pour off the liquid from flask in which carbon dioxide was made, make it alkaline with milk of lime obtained by shaking slaked lime and water in a jar and pouring at once. Let settle and filter. How does this remove iron and magnesium? Pass into the filtrate  $\text{CO}_2$  and boil. Why? Filter again if necessary and evaporate to dryness in a porcelain dish and heat. Expose a little of the calcium chloride to air till next period and observe again. Is it deliquescent? Dissolve the remainder in about 10 times its weight of water, and use as calcium chloride solution.

**118.—Comparative Solubilities of Salts of Ba, Sr, Ca, Mg: Carbonates:** To solutions of Ba, Sr, Ca and Mg chlorides from shelf add equal volumes of water then to each about one-fifth of its volume of ammonium chloride, and finally to each, ammonium carbonate. What compounds are precipitated? How could magnesium be separated from the other three metals? Add to its solution sodium phosphate, and see the tests for phosphoric acid (80) and Mg (128).

**119.—Chromates:** To solutions as under carbonates, but omitting Mg, add a little acetic acid then a solution of pure potassium chromate, or dichromate. How could barium be separated from strontium and calcium?

**120.—Sulfates:** To solutions of Ba, Sr, and Ca chlorides add a solution of magnesium sulfate and let stand for a few moments. How does this prove that Ba, Sr, and Ca sulfates are less soluble than magnesium sulfate? To fresh solutions of Ba and Sr chlorides add a solution of calcium sulfate. How do the results show that Ba and Sr sulfates are less soluble than calcium sulfate? To a solution of barium chloride add a solution of strontium sulfate and let stand a short time. How do we know that barium sulfate is less soluble than strontium sulfate? Arrange the sulfates in the order of their increasing solubility in water.

**121.—Calcium Oxalate:** To a solution of calcium chloride add an excess of ammonium carbonate, let stand a few moments and filter. To the filtrate and also to a solution of calcium sulfate add a solution of ammonium oxalate and let stand half an hour. State how you know that calcium oxalate is less soluble than calcium carbonate or calcium sulfate. Devise a scheme for the separation of Ba, Ca, Sr and Mg.

Calcium sulfate is present in many natural waters and causes "permanent hardness" in the sense that it is not precipitated by boiling, though on concentration by evaporation it forms a hard deposit on the boiler. To calcium sulfate solution add a solution of sodium carbonate. What two chemicals may be added to soften water showing

both temporary and permanent hardness?

Test the water of the laboratory for both sorts of hardness.

**122.**—Make analyses of a solution containing barium, strontium, calcium and magnesium according to the directions of Group IV; also, analyses of unknown solutions or solids which may contain these metals, and solutions or solids which may contain also metals of Group V and the ammonium radical.

### DECINORMAL SOLUTIONS, VOLUMETRIC ANALYSIS.

**123.**—Weigh accurately a small dish or beaker, add 2.65 grams to the weights and exactly balance with pure sodium carbonate. Dissolve the carbonate in water, transfer with rinsings of dish to a half liter flask, using a funnel and taking care that none of the solution is lost. Do not even lose some by removal on the stirring rod. Make up the volume to the mark with water, and mix by placing the thumb over mouth of flask and inverting several times. This is a decinormal solution of  $\text{Na}_2\text{CO}_3$ . Why? Transfer this solution to a bottle or larger flask and wash the graduated flask.

Measure in a small cylinder 7.5 c.c. pure con.  $\text{HCl}$  and dilute it to 700 c.c. and mix well. Fill a buret with the acid solution to well above the zero, fill the tip of buret and bring the surface to or below the zero. Read accurately at the lowest point of the meniscus. With a pipet (see 4) place 20 or 25 c.c. according to capacity of the pipet, of the sodium carbonate solution in a dish or beaker, add to it 2 drops of methyl orange. For comparison it is well to place beside it about 50 c.c. of water and add to it two drops of the indicator. From the buret run in the acid as rapidly as you wish to about 15 c.c. then a few drops at a time with stirring till the solution becomes faintly red as shown by comparison with the indicator in water. Make another titration, which should agree within a few tenths with the first.

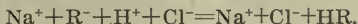
Divide the volume of the alkali by that of the acid which gives the decinormal concentration factor of the acid. Measure 500 c.c. of the acid and multiply by the factor, which will give the total volume to which the 500 must be made up with water to become decinormal. Why? Transfer the 500 c.c. to a larger vessel, add the necessary water, mix and titrate again against the alkali. They should neutralize each other volume for volume.

With these two standard deci-normal solutions the concentration of any other acid or alkali may be determined, or solutions of desired concentration may be made by the same method used in making the acid solution.

**124.**—In titrating weak acids methyl orange cannot be used; see next section. One must use a very weakly acid or neutral indicator, such as litmus, phenoltalein, congo red. But these are affected by

the carbonic acid from the carbonate and one must titrate the solution at the boiling point or use NaOH free from carbonate. Find the per cent of acid in vinegar by running it from a buret into a measured volume of the carbonate boiling and containing a few drops of phenoltalein, or use cold NaOH supplied by the instructor, instead of  $\text{Na}_2\text{CO}_3$ .

Methyl orange and phenolphthalein are weak, complicated organic acids. The following will give a correct, general idea of their action: Any strong acid sets free any weak acid from its salt. Let NaR be such a salt where R is the negative radical. Then,



In the case of phenolphthalein  $\text{R}^-$  gives the red color, while HR is colorless. Phenolphthalein is such a weak acid that even carbonic acid is strong enough to act in the same way as HCl in the equation and form HR. Hence when the stage in the titration represented by  $\text{HNaCO}_3$  is passed, and  $\text{H}_2\text{CO}_3$  is formed this acts as a relatively strong acid, forms HR and thus destroys the color. On the other hand methyl orange is a stronger acid than carbonic and the yellow color of its negative ion in  $\text{Na}^+ + \text{R}^-$  persists till there is a slight excess of HCl, when red HR is formed.

**125.**—The facts stated in 124 are well illustrated by titrating in the same solution both normal and bicarbonate by using different indicators, as follows:

Dissolve about 0.2 gram of normal sodium carbonate in 25 c.c. of water, without heating, add a few drops of phenoltalein, fill a buret with your deci-normal acid, read and run into the carbonate solution drop by drop near the end, till the pink color just disappears. The carbonate is now all  $\text{HNaCO}_3$ . Add a few drops of methyl orange, read the buret and run in the acid till the solution takes on a faint tinge of red, using the indicator in water for comparison as in 123. Read again and compare the volumes required to change the normal to the bicarbonate, and to neutralize the latter. Why are they approximately equal? Why are these carbonates alkaline, having no ion  $\text{OH}^-$ ? See 64.

## COPPER, SILVER.

### Copper.

**126.**—(a) Dissolve 5 grams copper chloride in 10 c.c. of con. HCl and 10 c.c. water; or (b) prepare a solution of the copper chloride by dissolving 5 grams copper sulfate and 2.5 grams common salt by heating with 10 c.c. of water in a test tube. When dissolved set the tube in cold water for several minutes. Pour off the solution from the separated sodium sulfate. Why is this formed? Now add to the solution 10 cc. con. HCl, let stand a few moments and filter off the salt. Why is salt thus formed? Whether (a) or (b) boil very gently the solu-



tion with 5 grams finely divided copper in a small flask, replacing evaporated liquid if necessary with dil. HCl. Continue till colorless or till a few drops poured into water gives no blue color. You now have  $\text{HCuCl}_2$ . Pour a part into water which decomposes it giving insoluble  $\text{CuCl}$ . Does this dissolve in ammonia? Compare with silver chloride. Put the ammonia solution in a white dish, stir and note that the cuprous ion is rapidly oxidized to cupric ion as shown by increasing blue color.

To a portion of the liquid from flask add an excess of NaOH. What is the red compound? See Fehling's solution (99). Heat a little of the white precipitate with Br water and give result in terms of ion formed. Expose some of the white  $\text{CuCl}$  on the filter to sunlight and note result after an hour.

There is no cupric but only cuprous iodide. To a few c.c. copper sulfate solution add a little potassium iodide solution, and test the solution for free iodine with starch paper. Add 1 c.c. carbon disulfide shake and let settle. Note color of the carbon disulfide.

Determine whether dilute sulfuric, hydrochloric and nitric acids give H by their action on copper and cadmium and explain results.

(c)—**Tests for Copper:** To half a test tube of water add a drop of solution of any cupric salt, and make alkaline with ammonia. The blue color is due to the complex ion  $\text{Cu}(\text{NH}_3)_4^{++}$ . To a like dilute solution of copper add a few drops of acid and a little potassium ferrocyanide. Dilute equal parts of each solution till the colors are just visible and state which test is the more delicate.

(d)—To dilute solutions of copper, cadmium and zinc preferably chlorides add  $\text{H}_2\text{S}$  in excess. Let settle and pour off most of the liquid in each case and add equal volumes of dil. HCl. Are the reactions with  $\text{H}_2\text{S}$  reversible? How may Cu and Zn be separated? To solutions of the same metals add an excess of NaOH and heat to boiling. For explanation see 127a and 128c. How may copper be separated from the other two elements?

To solutions of copper and cadmium add an excess of ammonia. Add to the copper tube KCN (dangerous) drop by drop till the blue color disappears. Add the same volume of KCN to the tube containing Cd. Now pass  $\text{H}_2\text{S}$  into each tube. How may Cu and Cd be separated?

### Silver.

127.—(a) To a little silver nitrate solution add drop by drop ammonia solution till the small amount of silver oxide at first formed is dissolved, forming the complex ion  $\text{Ag}(\text{NH}_3)_2^+$ . Add a little more ammonia and try to precipitate silver chloride with a small amount of



NaCl solution. Now add an excess of dilute nitric acid. What is precipitated and why?

To another portion of silver nitrate solution add sodium hydroxide solution which will precipitate mainly  $\text{Ag}_2\text{O}$ , but it is alkaline and behaves as though partially hydrated. A similar copper hydrated oxide is formed by adding an excess of NaOH to a solution of copper sulfate and heating to boiling. Try it. The compound is  $\text{Cu}(\text{OH})_2 \cdot 2\text{CuO}$ . Add ammonia to the tube containing the silver oxide till it just dissolves and then  $\text{H}_2\text{O}_2$ , which will give metallic silver. Prepare the same sort of a solution of silver oxide in ammonia, that is, containing the ion  $\text{Ag}(\text{NH}_3)_2^+$ , add 1 gram sodium potassium tartrate dissolved in a little water, warm the test tube and let stand. If silver is not deposited on the tube warm again. Note analogy of the complex silver ammonia ion to that of copper,  $\text{Cu}(\text{NH}_3)_4^{++}$  which is deep blue.

(b)—To four tubes containing silver nitrate add respectively a solution of a chloride, a bromide, an iodide and to the fourth drop by drop a solution of KCN (caution), till the silver cyanide at first formed is dissolved. Treat a little of each of the halides of silver with an excess of ammonia. Which are dissolved? Treat other small portions with a solution of sodium thiosulfate and shake till dissolved. Treat yet other portions with a solution of KCN till dissolved. How could you distinguish the three halides of silver by their color? How distinguish by their solubility in ammonia? What is formed when silver chloride dissolves in ammonia? What when it dissolves in KCN? Expose a little chloride to sunlight and observe color after a few minutes. Compare cuprous chloride and silver chloride as to the effects on them of sunlight and ammonia solution.

(c) To solutions of sodium phosphate, potassium chromate, sodium arsenite and sodium arsenate add silver nitrate. Try to dissolve portions of each precipitate in ammonia and in dil. nitric acid. Make careful records of all results for they are to be used in the qualitative testing for acid radicals.

### MAGNESIUM, ZINC, CADMIUM, MERCURY.

128.—(a) To solutions of magnesium, zinc and cadmium salts, preferably sulfates or chlorides add an excess of ammonium hydroxide. Some zinc and cadmium hydroxide are precipitated but in an excess of ammonia they form the complex ions  $\text{Zn}(\text{NH}_3)_4^{++}$  and  $\text{Cd}(\text{NH}_3)_4^{++}$  which are soluble. To show that only a part of the Mg is precipitated as hydroxide, filter it off and add acid sodium phosphate to the filtrate when more magnesium as  $\text{NH}_4\text{MgPO}_4$  will be precipitated. The prevention of complete precipitation as  $\text{Mg}(\text{OH})_2$  by ammonium hydroxide is due to the necessary accumulation of highly ionized ammonium salt as the reaction progresses. To show this first

add to a solution of magnesium salt ammonium chloride solution and then ammonium hydroxide. Also, precipitate  $\text{Mg}(\text{OH})_2$  with ammonia and then add ammonium chloride. In the first case no magnesium hydroxide was precipitated and in the second it dissolved.

The action of the ammonium salt which is highly ionized is to supply the common ion  $\text{NH}_4$  which forces the already slight dissociation of ammonium hydroxide to the left in  $\text{NH}_4\text{OH} \rightleftharpoons (\text{reversibly}) \text{NH}_4^+ + \text{OH}^-$  till there are not enough  $\text{OH}$  ions to form sufficient  $\text{Mg}(\text{OH})_2$  to exceed its solubility limit. Furthermore, the  $\text{NH}_4$  ions from the ammonium chloride or other ammonium salt unite with the  $\text{OH}$  ions associated with the  $\text{Mg}$  in solution to form the undissociated  $\text{NH}_4\text{OH}$ . This latter action is of the same sort as in the neutralization of a base by an acid in which the ion  $\text{H}$  of the acid unites with the  $\text{OH}$  of the base to form undissociated water.

This explanation applies to the solubility of several other hydroxides when ammonium salts are added and will be referred to later.

Prove that acid sodium phosphate alone will not completely precipitate  $\text{Mg}$  by adding to a magnesium solution an excess of phosphate, filtering and then adding to the filtrate ammonium chloride and ammonia. Make the corresponding salt of zinc,  $\text{NH}_4\text{ZnPO}_4$ .

(b) Burn a little  $\text{Mg}$  ribbon, place some of the oxide on moist turmeric paper and state whether it is alkaline. Burn a little zinc dust by heating and stirring in an iron crucible, and determine whether it has any alkaline property.

(c) Precipitate the hydroxides of  $\text{Mg}$ ,  $\text{Zn}$  and  $\text{Cd}$  by adding to their solutions  $\text{NaOH}$  a few drops at a time. Now add more  $\text{NaOH}$  to half of each and determine which are soluble in an excess. Dissolve the other half of each hydroxide by adding any dilute acid. With sodium hydroxide in excess zinc and cadmium hydroxides form  $\text{Na}_2\text{ZnO}_2$  and  $\text{Na}_2\text{CdO}_2$ , which resemble ordinary salts in form and properties. The hydroxide of  $\text{Zn}$  and  $\text{Cd}$  and many other elements are "amphoteric"; that is, they act like bases toward strong acids, and like weak acids toward strong bases. On the basis of the ion theory explain the dissolving of  $\text{Mg}(\text{OH})_2$  by  $\text{HCl}$ .

(d) To solutions of  $\text{Mg}$ ,  $\text{Zn}$ , and  $\text{Cd}$  add  $\text{H}_2\text{S}$  for several minutes. Which give sulfides? Shake and filter off half of each precipitate and to the filtrates add ammonia. Did the  $\text{H}_2\text{S}$  completely precipitate both the  $\text{Zn}$  and  $\text{Cd}$  as sulfides? To the other half of each precipitate obtained with  $\text{H}_2\text{S}$  alone add dilute  $\text{HCl}$  and finally con.  $\text{HCl}$  if needed to dissolve all the sulfides. Are the reactions of  $\text{Cd}$  and  $\text{Zn}$  salts with  $\text{H}_2\text{S}$  both reversible? Which one is most easily reversed? How may  $\text{Zn}$ ,  $\text{Mg}$  and  $\text{Cd}$  be separated?

### MERCURY

129.—Place 10 grams mercury in 4 c.c. con. nitric acid diluted with the same volume of water and let stand a day. Pour off liquid and dissolve the solid in water adding a little dilute nitric acid, letting the metallic mercury remain. This is a solution of mercurous nitrate, (a). Dissolve about 2 grams mercury in a few c.c. con. nitric acid, heat and if necessary add more nitric acid and heat till a drop of the solution in water gives no precipitate with HCl. Now dilute with about 50 c.c. water. This is mercuric nitrate, (b).

Treat small portions of (a) and (b) with NaOH in excess which gives  $\text{Hg}_2\text{O}$  and  $\text{HgO}$  and not the hydroxides. Compare the result with that obtained with silver nitrate and NaOH, with a cupric compound and NaOH cold and after boiling. Try ammonia on the solutions (a) and (b). No oxides or hydroxides are formed but with (a)  $\text{Hg}$  and  $\text{Hg}_2\text{N}(\text{NO}_3)$ . With (b) the same compound but no free  $\text{Hg}$ .

Treat a little of (a) with dil. HCl and determine whether the  $\text{HgCl}$  is soluble in an excess of HCl or in nitric acid. Try the action of ammonia which gives black  $\text{Hg}$ .  $\text{HgNH}_2\text{Cl}$ . How may mercury in the mercurous condition be separated from silver? Oxidize a little of solution (a) to (b) by adding Br water till the red color persists, boiling out excess of Br. Prove that only mercuric mercury is present by adding dil. HCl.

To small portions of (a) and (b) add a solution of KI drop by drop giving green  $\text{HgI}$  and red  $\text{HgI}_2$ . To the latter add an excess of KI which will dissolve forming a double salt,  $\text{HgI}_2 \cdot 2\text{KI}$ .

To a very dilute solution of stannous chloride add a solution of mercuric chloride which gives  $\text{HgCl}$  while  $\text{SnCl}_4$ , stannic chloride, remains in solution. This is a good test for either  $\text{Hg}$  or  $\text{Sn}$ . What must be the valence of each ion when tested for?

To (a) and (b), and to solutions of  $\text{Pb}$ ,  $\text{Cu}$ ,  $\text{Cd}$  add an excess of  $\text{H}_2\text{S}$ . Let settle, pour off the liquid in each case and try to dissolve the precipitates by boiling with dilute nitric acid. How may mercury be separated from the other metals? Determine whether  $\text{HgS}$  will dissolve in ammonium sulfide. How may mercury be separated from  $\text{As}$ , and  $\text{Sb}$ .

### TIN.

130.—Dissolve most of 2 grams of tin by heating with 10 c.c. con. HCl, best in a small flask on the water bath. Pour off half of the solution into a dish and add 50 c.c. of water to the flask and use the solution as stannous chloride, (a). Heat to boiling the solution in the dish and add con. nitric acid a few drops at a time till a drop in a



little water gives no precipitate with mercuric chloride. Add 50 c.c. of water forming a suitable solution of stannic chloride, (b).

To small portions of (a) and (b) add a few drops of NaOH, then add in excess. Are these hydroxides "amphoteric"? To fresh portions of the tin solutions add yellow ammonium sulfide, at first only a few drops, then an excess with heating, but do not boil. The  $\text{SnS}$  and  $\text{SnS}_2$  at first formed, should dissolve. Now add HCl in excess which will reprecipitate the tin sulfide,  $\text{SnS}_2$  from each solution. What other sulfides dissolve in ammonium sulfide? How may the tin sulfides be separated from those of copper, lead, mercury?

To a little of (a) add a solution of mercuric chloride which will give insoluble  $\text{HgCl}_2$ . Try (b) with mercury chloride. Now reduce to the stannous condition the Sn in a portion of (b) by persistent heating with finely divided iron, filter and add mercuric chloride. This is a good test for either Hg or tin. In what condition of oxidation must each be?

To a portion of (a) add a few drops of gold chloride which will give colloidal gold, the purple of Cassius, a good test for gold.

### LEAD.

**131.**—To a dilute solution of lead acetate or nitrate add an excess of NaCl solution. Before the lead chloride settles pour off one half and boil, adding more water if necessary and boiling till it all dissolves. Let the other half stand 5-10 minutes, filter and to the filtrate add dil. sulfuric acid. What proof here that lead sulfate is less soluble than lead chloride? Filter off the lead sulfate and pass into filtrate  $\text{H}_2\text{S}$ . Which is less soluble, lead sulfate or lead sulfide? From a dilute solution precipitate lead chloride and prove that it is soluble in HCl if added in large excess. Prove in the same way that lead sulfate is soluble in nitric acid. These facts must be kept in mind in the analysis of Group II. Try to dissolve lead chloride in ammonia. Devise a scheme for the separation of Ag, Hg (mercurous) and Pb.

**132.**—To a solution of lead acetate add a solution of sodium carbonate till alkaline. The precipitate is a basic carbonate similar to "white lead." Shake a solution of lead acetate with  $\text{PbO}$ , filter and pass through carbon dioxide which will give much the same compound.

Mix 5 c.c. con. nitric acid and 5 c.c. water, heat and add a little at a time about 2 grams red lead,  $\text{Pb}_3\text{O}_4$ . The brown product is lead dioxide,  $\text{PbO}_2$ . Filter a few drops of the liquid and add dil.  $\text{H}_2\text{SO}_4$ . Is there lead in solution? To show the oxidizing power of lead dioxide add to it and the rest of the liquid a few drops of any salt of manganese and boil persistently. Let the solid matter settle and note deep red color due to permanganic acid,  $\text{HMnO}_4$ .



133.—To 20 c.c. of the lead acetate solution of the laboratory add 80 c.c. pure water, place in flask and with a thread suspend in it a folded strip of zinc, about 5 grams, and let stand till next period. Examine the "lead tree," and test the solution for lead and zinc. Which metal is most electropositive?

### ALUMINIUM.

134.—Dissolve a few tenths of a gram of Al in con. HCl and dilute to a test tube full, and use where  $\text{AlCl}_3$  is required (a). Dissolve another small amount of Al in a few c.c. of NaOH warming, which gives sodium aluminate,  $\text{Al}(\text{ONa})_3$ , (b). What gas is given off in each case?

To a little of (a) add ammonia in excess. To (a) add drop by drop NaOH till a permanent precipitate is obtained. Dissolve one-half of it by adding HCl and the other half with an excess of NaOH. Is  $\text{Al}(\text{OH})_3$  amphoteric? In what two ways may it ionize? To (b) add ammonium chloride till the precipitate is permanent, and account for its formation. How could you separate Al and Zn?

To portions of (a) add in excess sodium carbonate, and ammonium sulfide and account for the precipitation of  $\text{Al}(\text{OH})_3$  in each case?

135.—By heating dissolve 15 grams of aluminium sulfate,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  in 50 cc. water, stir in the calculated weight of ammonium sulfate to make ammonium aluminium alum  $(\text{NH}_4)_2\text{Al}_2(\text{SO}_4)_4$ , and when all is dissolved filter into a crystallizing dish while hot. Let a drop or two of filtrate fall on a watch glass, let the water evaporate and examine the crystals with a microscope. Examine the crystals in dish, dissolve a few and test the solution with blue litmus paper. Why are the solutions of Al salts acid? See 63.

### CHROMIUM.

136.—Chromate Ion to Chromium Ion: Dissolve in a dish 10 grams potassium dichromate in 50 c.c. water with heat and let cool. Add 10 c.c. con. sulfuric acid and then a little at a time 50 per cent alcohol heating if necessary to start the reaction. Continue the addition of alcohol till the solution has a green color, a few drops in much water showing no brown. Avoid a large excess of alcohol. Set aside two-thirds of the solution and examine the crystals of chrome alum at the next laboratory period. Dilute the other third with 20 times its volume of water and use it below. One molecule of the dichromate is reduced by the oxidation of three molecules of alcohol to aldehyde,  $\text{CH}_3\text{COH}$ . With aid of text write the equation. What was the action of  $\text{H}_2\text{S}$  and of  $\text{SO}_2$  on acidified solutions of  $\text{K}_2\text{Cr}_2\text{O}_7$ ?

Treat a portion of your solution of chrome alum with an excess of ammonia. How separate Cr and Zn? Try to dissolve a little of the remaining precipitate with  $\text{NH}_4\text{Cl}$ . How separate Cr from Mg? To an-

other portion of chrome alum solution add an excess of NaOH and boil. How separate Cr and Al? Is  $\text{Cr}(\text{OH})_3$  amphoteric? Try portions of your chrome alum with solutions of sodium carbonate and ammonium sulfide. In each case the hydroxide is precipitated as in the case of Al.

**137.—Chromium Ion to Chromate Ion:** To a few c.c. of chromium nitrate or chloride solution in a dish add an equal volume of NaOH. Stir into it gradually 2 grams sodium dioxide and heat to boiling. Filter if necessary, acidify a little of the filtrate with acetic acid being sure of an excess by testing, and add barium chloride. To a little dilute solution of sodium dichromate add acetic acid and barium chloride and compare precipitates.

**138.—Dichromate to Chromate:** (a) Dissolve 5 grams sodium dichromate in 25 c.c. water in a dish, add slowly with stirring NaOH till the solution becomes yellow. Evaporate till the salt crystallizes on cooling.

(b)—**Chromate to Dichromate:** Dissolve 10 grams sodium chromate in 25 cc. water and add the calculated weight of con. sulfuric acid, that is, one molecule of acid to two of the chromate. Evaporate till the dichromate crystallizes out on cooling.

(c)—**Chromium Trioxide:** Dissolve 2 grams potassium dichromate in 5 c.c. water by heat, cool till it begins to separate then drop con. sulfuric acid directly upon the surface of the liquid in test tube till the precipitate formed does not quite dissolve. Heat to dissolve most of it, note the escape of some oxygen, set in rack to cool and observe crystals of  $\text{CrO}_3$  in an hour.

**139.—Chromium Oxychloride:** In a retort place 3 grams dichromate, 2 grams NaCl and 15 cc. con.  $\text{H}_2\text{SO}_4$ . Heat and collect the oxychloride as you did nitric acid. What does it look like? Dissolve some of it in water, add an excess of NaOH, then an excess of acetic acid and finally barium chloride. What is the precipitate?

**140.—Test for Chromate Ion:** To two small portions of a chromate solution add acetic acid then barium chloride and lead acetate respectively. To a neutral solution of a chromate add silver nitrate. Divide into two portions. In one try the solubility of the silver chromate in ammonia and in the other with dil. nitric acid. A third test is the reduction of chromate ion to chromium ion with change from yellow or red to green as in 136.

## IRON, NICKEL, COBALT.

### Iron.

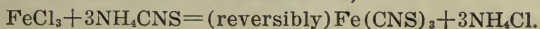
**141.—**Dissolve most of about 1 gram of card teeth in con. HCl diluted with an equal volume of water. Pour one half in a dish. Dilute the other half to a test tube full leaving in it the undissolved iron. This

is ferrous chloride,  $\text{FeCl}_2$ , solution (a). Heat the half in the dish and with stirring add a little con. nitric acid at a time till the black precipitate at first formed dissolves and a drop of the solution in a little water gives no blue color with potassium ferricyanide. Dilute to a test tube full. It is ferric chloride,  $\text{FeCl}_3$  (b).

Treat small portions of (a) with an excess of ammonia,  $\text{NaOH}$ , sodium carbonate,  $\text{H}_2\text{S}$ , ammonium sulfide. The first and second give ferrous hydroxide  $\text{Fe}(\text{OH})_2$ , changing in air to ferric hydroxide  $\text{Fe}(\text{OH})_3$ ; the third gives ferrous carbonate. Hydrogen sulfide has no effect, but ammonium sulfide gives black  $\text{FeS}$ . Treat small portions of (b) with the same reagents in excess. Ammonia,  $\text{NaOH}$  and sodium carbonate give ferric hydroxide.  $\text{H}_2\text{S}$  reduces ferric to ferrous iron with the separation of sulfur. Why does it not precipitate iron sulfide? Is either hydroxide amphoteric? Try to dissolve ferrous and ferric hydroxides with ammonium chloride. Compare the action of sodium carbonate and ammonium sulfide on ferric iron, aluminium and chromium solutions. Devise ways to separate iron from  $\text{Al}$ ,  $\text{Cr}$ ,  $\text{Cu}$ ,  $\text{Mg}$ ,  $\text{As}$ .

**142.**—Treat portions of (a) and (b) with solutions of potassium ferrocyanide, potassium ferricyanide, ammonium sulfocyanide and tabulate results as tests for ferrous and ferric iron.

The following is a fine example of a reversible reaction and illustration of the influence of the common ion: To a test tube nearly full of water add about 5 drops of ammonium sulfocyanide and the same amount of ferric chloride. The reaction is,



Divide the red solution in four test tubes. To one add more of the ferric chloride, to the second more of the sulfocyanide, to the third ammonium chloride, and compare colors with that of the fourth. Refer to 62 and to text book and explain fully.

**143.—Double Salts:** (a) Dissolve in 50 cc. water by heat 10 grams ferrous sulfate and the calculated amount of ammonium sulfate to make ammonium ferrous sulfate and filter hot into a crystallizing dish. Examine crystals in dish, also let a drop cool on watch glass and use microscope. This is Mohr's salt,  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .

(b) To make iron alum dissolve 15 grams ferrous sulfate in 25 c.c. water in dish, also the calculated amounts of ammonium sulfate and con. sulfuric acid. Now heat and add slowly with stirring, con. nitric acid till a drop diluted shows no ferrous iron. Set aside to crystallize, giving  $(\text{NH}_4)_2\text{Fe}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$ .

### NICKEL AND COBALT.

**144.**—From nickel and cobalt chlorides or nitrates precipitate their hydroxides with  $\text{NaOH}$  in excess. Try to dissolve portions of the hydroxides in excess of  $\text{NaOH}$  with heating. Are they amphoteric? Try



to dissolve other portions of the hydroxides with ammonium chloride. How may these metals be separated from ferric iron, aluminium, chromium?

Try to precipitate the sulfides of Ni and Co with  $\text{H}_2\text{S}$ , then with  $\text{H}_2\text{S}$  and ammonia or with ammonium sulfide. Try to dissolve the sulfides with dil.  $\text{HCl}$ . How may Ni and Co be separated from Zn, Fe, Sb and the metals of groups I and II?

To 1 to 2 c.c. of solutions of Ni and Co add  $\text{NaOH}$  with shaking till the hydroxides are just permanent. Add to each tube acetic acid in slight excess, then to each 10 cc. of a solution of potassium nitrite and let stand. The precipitate is  $\text{K}_3\text{Co}(\text{NO}_2)_6$ . How may Co be separated from Ni?

Again precipitate the hydroxides of the two metals from 1 to 2 cc. of their solutions avoiding a large excess of  $\text{NaOH}$ . Add to each a solution of  $\text{KCN}$  (dangerous) till the precipitates just dissolve. Now add to each about 1 c.c. of  $\text{NaOH}$  and bromine water till it colors them permanently red. A black precipitate of nickelic hydroxide should be obtained.

### MANGANESE

**145.**—To a few cc. of a solution of manganous salt, as  $\text{MnCl}_2$ , add ammonia in excess and to another portion  $\text{NaOH}$  in excess. Does the  $\text{Mn}(\text{OH})_2$  redissolve? How may Mn be separated from Zn, Al, Cu, Ag?

Add to one fresh portion of the solution ammonia in excess then ammonium chloride, and to another portion add ammonium chloride then ammonia. Compare the results with those obtained with Mg and the same reagents. To one of these solutions add ammonium sulfide and to the other hydrogen sulfide. How could you separate Mn and Mg? Try to dissolve the sulfide in dil.  $\text{HCl}$ . How may Mn be separated from Cu, Hg, As, Sb?

To a manganese solution add ammonium chloride, ammonia, and sodium phosphate. Compare result with the action of these reagents on solutions of Zn and Mg.

**146.—Permanganic Acid and Permanganate:** To about 2 c.c. of a solution of any manganous salt add an equal volume of con. nitric acid, then about 1 gram of red lead or lead dioxide, and heat some time at the boiling point. Let the undissolved matter settle and note red color of permanganic acid. This is a good test for Mn. Pour off a little of the clear solution into water to see color better.

(b) Melt in an iron crucible 5 grams solid  $\text{KOH}$  and 2.5 grams potassium chlorate, and stir in gradually 2 grams  $\text{MnO}_2$ . Heat with stirring till the mass turns solid and raise the temperature with full burner flame, and continue 5 minutes. When the mass is cold dissolve out by heating with the crucible nearly full of water. Pour the solution into a large test tube and let settle. To one portion of the



green solution of potassium manganate,  $K_2MnO_4$ , add dilute sulfuric acid till it just turns red forming potassium permanganate,  $KMnO_4$ . Try changing the manganate to permanganate in another portion by passing through it carbon dioxide, and in a third by diluting it with much water.

**147.**—Dissolve about one-fourth gram of oxalic acid in water, add 5 c.c. dil. sulfuric acid, heat to about 80 degrees and add a little at a time a solution of potassium permanganate till the color becomes permanent. Dissolve about one-half of a gram of ammonium ferrous sulfate (143a), add sulfuric acid and permanganate as above. These reactions illustrate oxidation by permanganic acid and are much used in quantitative analysis. Write the equations, assuming that the oxalic acid is oxidized to water and  $CO_2$  and the  $FeSO_4$  to  $Fe_2(SO_4)_3$ .

### QUALITATIVE SEPARATION OF THE METALS

The following scheme of analysis is prepared for first year students in chemistry to be used in the separation of the common metals. Provision is not made for every contingency. For example, it is assumed that the ions to form insoluble phosphates in Group III are not present.

**148.—Group I; Ag, Pb, Hg:** Determine with test paper whether the solution is neutral or only slightly acid. If neutral add one-tenth of its volume of HCl, sp. gr. 1.12. If strongly acid, neutralize with ammonium hydroxide and then add the HCl. The purpose is to have enough acid to prevent the precipitation of  $BiOCl$  in this group and  $ZnS$  in the next, and not enough to prevent the precipitation of  $SnS$  and  $CdS$  in group II.

If no precipitate is formed pass to group II. If one is formed let remain a few moments and filter. Set aside the filtrate (1) for group (II). Wash twice the precipitated chlorides of Ag, Pb,  $Hg_2$  with small portions of cold water. Now pour through the filter a half test tube full of boiling water. Boil and pour through again. Add to one-half of filtrate dil. sulfuric acid and let stand. A white precipitate shows lead sulfate. To the other add potassium chromate. A yellow precipitate is lead chromate.

Treat the remaining precipitate on the filter with about 5 c.c. of  $NH_4OH$ . Pass it through a second time. Now add to this filtrate an excess of dil. nitric acid, making sure of an excess by mixing and testing.  $AgCl$  is obtained if silver is present. The blackening of the residue left on filter when ammonia was added shows  $Hg_2$  present, the black substance being Hg and  $HgNH_2Cl$ .

Write equations for all reactions that occur in the analysis of Group I.

**149.—Group II; As, Sb, Sn, Hg, Pb, Bi, Cu, Cd:** Heat filtrate (1) from group (I) nearly to boiling and pass in  $H_2S$  for about 10 minutes keep-

ing the temperature near the boiling point so as to precipitate arsenic from arsenates if present. Now let cool, add an equal volume of water and pass in the gas for several minutes to insure the complete precipitation of cadmium and tin. Even then it is well to let the precipitate settle, pour off a few drops of the liquid, add water and more gas. Disregard a white precipitate which might be  $\text{ZnS}$ . When assured that the precipitation is complete let the precipitate settle and pour off the solution through a filter. At once boil it to expel  $\text{H}_2\text{S}$  and set it aside as filtrate (2) for group III.

Wash the precipitate four times by decantation; that is, pour upon it hot water, boil, let settle completely and pour off the wash water. Drain carefully the last time since much water present will dilute the nitric acid to be used.

If it is known that As, Sb and Sn are absent omit the bracketed directions, and boil with dil. nitric acid as directed after the bracketed lines. If not known whether they are present or not proceed as directed within the brackets.

[Now heat a small portion of the washed precipitate with about 3 c.c. of yellow ammonium sulfide, best in a dish on a water bath with stirring. In any case **do not boil**. Filter off the solution and add to filtrate dil.  $\text{HCl}$  till acid throughout, and boil. If only white finely divided sulfur is precipitated As, Sb and Sn are absent. In this case proceed to boil the remainder of the precipitate with nitric acid as after the brackets. If, however, a flocculent yellowish precipitate is obtained one or more of the above metals are present. Treat the remainder of the washed precipitate with ammonium sulfide as directed for the small portion, filter and set aside to be examined for As, Sb and Sn, as described within the brackets below.

The residue consisting of sulfides undissolved by ammonium sulfide must be well washed on the filter. [Punch through the tip of the filter, wash the sulfides into a test tube and let settle.] Pour off as much as possible of the water, add about 10 c.c. dil. nitric acid and boil persistently. All the sulfides except that of Hg are dissolved. A floating residue of S often remains and is to be disregarded. A heavy residue which settles at once to the bottom must be tested for Hg. Filter off the  $\text{HgS}$ , add to the filtrate 10 cc. dil. sulfuric acid and begin its evaporation in a porcelain dish. To confirm the presence of Hg dissolve the sulfide on the filter by pouring upon it about 3 c.c. of hot con.  $\text{HCl}$  to which a little potassium chlorate has been added. Heat and pass through again if necessary. Add to the solution bromine water till the color of Br persists, boil out the excess and add a few drops of a solution of stannous chloride. A white precipitate turning to gray and perhaps to black shows Hg present.

Evaporate the nitric acid solution containing the other metals till

heavy white fumes of sulfuric acid freely come off. The evaporation must be carried far enough to expel all the nitric acid. (See 131) Let the dish and contents cool, then add 10 c.c. of water and let stand 5 minutes. A white precipitate shows lead sulfate. Filter it off and add to filtrate an excess of ammonium hydroxide, making sure of an excess by shaking to mix and then testing with turmeric paper. A white precipitate shows Bi but its presence should be confirmed thus: Filter it off. Dissolve on the filter in a few drops of con. HCl, evaporate off nearly all of the acid. (Why?) Pour into much water. A white cloud is  $\text{BiOCl}$ .

The filtrate from the bismuth hydroxide is blue if copper is present. If copper is absent add hydrogen sulfide to the filtrate which will give yellow  $\text{CdS}$  if Cd is present. If the blue color shows Cu present test for Cd by one of the following:

(a) Add to the blue solution a solution of potassium cyanide (very poisonous) till the blue color disappears, then hydrogen sulfide which will give yellow  $\text{CdS}$  if Cd is present.

(b) Add to the blue solution dil. sulfuric acid till colorless then card teeth or steel wool and boil for some time. The iron removes the Cu. Why? Filter, be sure that the filtrate is still acid. If not add a slight excess of sulfuric acid and then  $\text{H}_2\text{S}$  which will give yellow  $\text{CdS}$  if Cd is present.

[To the  $(\text{NH}_4)_2\text{S}$  solution containing As, Sb and Sn, add dilute HCl in excess, which re-precipitates the sulphides if present. A precipitate is always produced owing to the separation of sulphur. If the sulphides are present, however, the precipitate is more highly colored and somewhat flocculent. Filter and wash the sulphides, carefully remove to a test tube and heat with strong HCl.  $\text{Sb}_2\text{S}_3$  and  $\text{SnS}_2$  are dissolved, while  $\text{As}_2\text{S}_3$  is not. Dissolve the  $\text{As}_2\text{S}_3$  in hot, strong HCl and  $\text{KClO}_3$ , boiling if necessary, best in a small flask placed in the evaporating closet. Add to the solution  $\text{NH}_4\text{OH}$  in excess then  $\text{NH}_4\text{Cl}$ , filter if not clear and add  $\text{MgSO}_4$ , which will give on standing a precipitate of  $\text{NH}_4\text{MgAsO}_4$  if As is present.

Boil persistently the filtrate from the arsenic sulfide with card teeth. The Sb is deposited on the card teeth from which it can be detached in scales by stirring with a glass rod, and the tin remains in solution as  $\text{SnCl}_2$ . Filter off the antimony and test the filtrate for tin with  $\text{HgCl}_2$ . Wash the antimony thoroughly, dissolve on the filter with a very little aqua regia, dilute with 10 to 20 times its volume of water and add  $\text{H}_2\text{S}$  which will give orange yellow  $\text{Sb}_2\text{S}_3$ ].

Write equations for all reactions involved in Group II assuming that all metals are present in the beginning as chloride.

**150—Group III: Fe, Al, Cr, Co, Ni, Mn, Zn:** To a small portion of filtrate 2 from Group II add ammonia in excess as proved by shak-



ing and testing. If a precipitate is formed one or more of the metals, Fe, Al, Cr are present. If no precipitate is formed add  $\text{H}_2\text{S}$ ; or, if a precipitate was formed by ammonia filter it off and add  $\text{H}_2\text{S}$  to the filtrate. If  $\text{H}_2\text{S}$  causes a precipitate which is not black Co, and Ni are absent. A black precipitate means either Co or Ni or both and they may mask Mn and Zn. By making these preliminary tests and attention to the following much work and time may be saved.

If no precipitate was formed by either ammonia or  $\text{H}_2\text{S}$  proceed with the rest of the filtrate to Group IV. If a precipitate was formed only with ammonia there is no need to test for Co, Ni, Mn, Zn. In this case add ammonia to all the filtrate, filter off the hydroxides of Fe, Al, Cr, and save the filtrate for Group IV, omitting the addition of  $\text{H}_2\text{S}$  below and also that part of the directions applying to Co, Ni, Mn, Zn. If  $\text{H}_2\text{S}$  made a precipitate while ammonia did not Al and Cr are absent but Fe may be present if the precipitate was black.

The following scheme provides of course for the presence of all these metals:

To filtrate (2) from Group II add ammonia in slight excess testing after shaking, then add about 2 c.c. more. Heat the solution in a flask or large test tube nearly to boiling and pass in  $\text{H}_2\text{S}$ . Shake and heat frequently to make the precipitate granular and more easily filtered and washed. When the precipitation is apparently completed filter a small portion and pass into it more gas. If more precipitate forms add more  $\text{H}_2\text{S}$  to the whole and thus proceed till complete precipitation is attained.

Filter through a fluted filter and wash with hot water. Boil the filtrate (3) till all hydrogen sulfide is expelled, filter it and set aside for Group IV. As soon as the precipitate produced by  $\text{H}_2\text{S}$  is sufficiently washed, (about two funnels full of hot water), punch through the tip of the filter and wash most of the precipitate into a small flask with a fine stream of water from the wash bottle. At once add considerable excess of dil.  $\text{HCl}$ . Only  $\text{NiS}$  and  $\text{CoS}$  remain undissolved. Filter, reserve filtrate for B and test for Ni and Co in A.

A. Dissolve the  $\text{NiS}$  and  $\text{CoS}$  in the filter in about 3 c.c. of aqua regia and evaporate the solution nearly to dryness in a dish. Add about 4 c.c. water then  $\text{NaOH}$  drop by drop with shaking till a permanent precipitate is obtained. Avoid a large excess of  $\text{NaOH}$ . Divide the liquid and suspended precipitate into two portions, and test for Co and Ni as follows:

1. To one portion add about 2 cc. acetic acid, 30 per cent, and 15 c.c. of a 25 per cent solution of potassium nitrite and let the solution stand half an hour. A yellowish, white granular precipitate is  $\text{K}_2\text{Co}(\text{NO}_2)_6$ .



2. To the other half add a solution of potassium cyanide (dangerous) drop by drop till the precipitate just dissolves. It is essential to avoid a large excess. Warm the solution, add about 5c.c. NaOH and then bromine water till the color of Br persists. A black precipitate often forming after some time is  $\text{Ni}(\text{OH})_2$ .

B. Evaporate the filtrate from the  $\text{CoS}$  and  $\text{NiS}$  nearly to dryness, add about 5 c.c. water, make strongly alkaline with NaOH and add gradually with stirring about 2 grams of sodium dioxide. Boil a few minutes, add water and filter off the Fe and Mn hydroxides. Save the filtrate for C and wash the precipitate. To test for Mn make a bead of sodium carbonate, while hot touch to powdered  $\text{KClO}_3$ . Let cool, take up with it a little of the precipitate and fuse with the blow-pipe. A green bead shows Mn present. To confirm the presence of Mn and test for Fe remove a small portion of the precipitate from the filter, dissolve it in dilute nitric acid and add a solution of potassium ferrocyanide which will give a dark blue color if Fe is present. Now pour upon the remaining precipitate about 3 c.c. of hydrogen dioxide and then add 10 c.c. nitric acid, sp. gr. 1.2, which means practically 1 vol. of pure concentrated acid diluted with 2 parts of water. Warm and pass through again if necessary. To this solution add a little at a time 2-4 grams of lead dioxide or red lead and heat to gentle boiling for a few moments. Let the suspended matter settle when the liquid above it will be colored red by permanganic acid if Mn is present.

C. To the filtrate from the Fe and Mn hydroxides which may contain Al, Cr and Zn, add con. nitric acid in slight excess testing with litmus paper. Add 5 c.c. ammonium chloride, heat and add ammonia in slight excess as shown by test after stirring. A white flocculent precipitate shows aluminium hydroxide. Filter it off and acidify the filtrate with acetic acid, mixing and testing with litmus paper. The liquid is yellow if chromate radical is present. Add barium chloride which will give yellow  $\text{BaCrO}_4$ . The  $\text{BaCl}_2$  must be added in excess to remove all the  $\text{CrO}_4$  which would interfere with the test for Zn. Filter and pass through several times if necessary. The clear filtrate should not be yellow. If it is add more  $\text{BaCl}_2$  and filter again. To the clear, colorless filtrate add  $\text{H}_2\text{S}$  which will give an evident, white precipitate if Zn is present. Hydrogen sulfide always produces an opalescence at this point and this is to be disregarded.

#### GROUP IV.

151.—If the analysis is being carried through all the groups the solution used will be filtrate (3), in which case it should be made slightly acid with dilute HCl, evaporated to two-thirds of its volume, and ammonium hydroxide added till alkaline then ammonium carbonate. If the solution is an original one, add ammonium chloride, am-

monium hydroxide till alkaline then ammonium carbonate till the precipitation is complete. To determine this heat the solution nearly to boiling, let settle and add a few drops of the carbonate to the clear solution. Filter and to a small portion of the filtrate add sodium phosphate which will give  $(\text{NH}_4)\text{MgPO}_4$  if magnesium is present. Reserve the remainder of the filtrate (4) for Group V. Wash the carbonates on the filter and dissolve by pouring upon the filter not more than 5 c.c. of acetic acid, letting it run through into a clean tube. Run through several times if necessary to dissolve all the carbonates. To a small portion of the acetic acid solution add twice its volume of a saturated solution of calcium sulfate. Note carefully whether the precipitate is formed at once or only after a few seconds. Proceed according to one of the following as required, using the rest of the acetic acid solution:

(a) If no precipitate was formed, to the remainder of the acetic acid solution add ammonia in excess and ammonium oxalate which will precipitate calcium oxalate.

(b) If the precipitate was slowly formed, only Sr and Ca can be present. To the acetic acid solution add a solution of ammonium sulfate and let stand. Filter off the strontium sulfate, and to the filtrate add ammonium hydroxide till alkaline then ammonium oxalate which will precipitate  $\text{CaC}_2\text{O}_4$ , if Ca is present.

(c) If the precipitate with  $\text{CaSO}_4$  was immediate Ba is present, and the other two may be. To the acetic acid solution add an excess of pure potassium chromate solution. Filter off the barium chromate. Make the filtrate alkaline with ammonia and add ammonium carbonate, which will precipitate Ca and Sr carbonates if they are present. Filter off the carbonates, wash till most of the excess of chromate is removed, and dissolve on the filter with acetic acid. Test a small portion of the filtrate with  $\text{CaSO}_4$ . If no precipitate forms on long standing Sr is absent and Ca should be tested for as in (a). If Sr is present remove it from the remainder of the acetic acid solution with ammonium sulfate, let stand 5 minutes, filter and test filtrate for Ca as in (b).

### GROUP V.

152.—Evaporate a part of filtrate (4) to dryness in a porcelain crucible; heat till all ammonium salts are expelled, and test with the spectroscope as directed in lecture for Na, K and Li. If uncertain as to the spectrum lines and flame colors, compare with spectra of the known substances.

To test for  $\text{NH}_4$ , place in a porcelain crucible a small amount of lime, add enough of the original solution to moisten it, cover with a watch glass with a strip of moist turmeric paper on the under side, and warm gently. If  $\text{NH}_4$  be present,  $\text{NH}_3$  will be evolved and can be recognized by its action on the turmeric paper and by its odor.

## APPENDIX

### 153.—Atomic Weights of the Common Elements:

Aluminum.....	Al	27.1	Lead.....	Pb	207.20
Antimony.....	Sb	120.2	Lithium.....	Li	6.94
Arsenic.....	As	74.96	Magnesium.....	Mg	24.32
Barium.....	Ba	137.37	Manganese.....	Mn	54.93
Bismuth.....	Bi	208.0	Mercury.....	Hg	200.6
Boron.....	B	11.0	Molybdenum.....	Mo	96.0
Bromine.....	Br	79.92	Nickel.....	Ni	58.68
Cadmium.....	Cd	112.40	Nitrogen.....	N	14.01
Calcium.....	Ca	40.07	Oxygen.....	O	16.00
Carbon.....	C	12.00	Phosphorus.....	P	31.04
Chlorine.....	Cl	35.46	Platinum.....	Pt	195.2
Chromium.....	Cr	52.0	Potassium.....	K	39.10
Cobalt.....	Co	58.97	Silicon.....	Si	28.3
Copper.....	Cu	63.57	Silver.....	Ag	107.88
Fluorine.....	F	19.0	Sodium.....	Na	23.00
Gold.....	Au	197.2	Strontium.....	Sr	87.62
Hydrogen.....	H	1.008	Sulphur.....	S	32.06
Iodine.....	I	126.92	Tin.....	Sn	118.7
Iron.....	Fe	55.84	Zinc.....	Zn	65.37

### 154.—Vapor Pressure of Water in Millimeters of Mercury:

Degrees C.	Pressure	Degrees C.	Pressure
15	12.7	26	25.0
16	13.6	27	26.5
17	14.5	28	28.1
18	15.4	29	29.8
19	16.4	30	31.6
20	17.4	31	33.4
21	18.5	32	35.4
22	20.0	33	37.4
23	20.9	34	39.6
24	22.2	35	41.9
25	23.5		

















